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RECOVERY OF URANIUM FROM SLAG FROM THE ELECTRIC FURNACE PRODUCTION OF PHOSPHORUS*

by

H. Z. Cammack and G. L. Bridger

ABSTRACT

When phosphate rock is reduced to elemental phosphorus with coke in the electric furnace process, the uranium in the phosphate rock virtually all goes into the by-product slag. It is estimated that approximately 300 tons of uranium is potentially recoverable per year from this use of phosphate rock.

Previous work at Battelle Memorial Institute, Mound Laboratory, and the Tennessee Valley Authority did not result in an economic process for the recovery of uranium from electric furnace slags. The present investigation included thermal reductions with alkaline earth metals, high temperature liquid-liquid extraction with molten extractants, solubilizing fusions, magnetic separations, and leaching with various solutions. As an adjunct to the high temperature liquid-liquid extraction studies, the solubility of uranium in antimony, bismuth, lead, silver and tin were further studied, to corroborate and extend existing data.

Radioassay methods of analysis were developed for the raw furnace slags and residues from the various experimental treatments. A fraction of the slag residues were checked for uranium using a colorimetric procedure. All binary alloys resulting from the uranium solubility study were analyzed with colorimetric procedures developed during the course of the investigation.

The results of the thermal reduction experiments do not indicate a concentration of uranium in either layer of mechanically partitioned slag residues. Bismuth, lead and manganese appear to extract the most uranium from furnace slags by a single contact of the metal with the slag. In all high temperature extraction treatments, about 50 per cent of the uranium appeared amenable to extraction. The addition of calcium, magnesium, aluminum and potassium to the melt with iron

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*This report is based on a Ph.D. thesis by H. Z. Cammack, submitted August, 1955, to Iowa State College, Ames, Iowa. This work was performed under contract with the Atomic Energy Commission.

extractant appeared to improve the uranium extraction. Iron sulfides were found to extract approximately 45 per cent of the uranium from the slags by a single contact with the slags.

Contacting one portion of furnace slag with three successive portions of iron-calcium, bismuth or iron sulfide extractant did not improve the total uranium extraction from the slag to above 50 per cent. Contacting one portion of these extractants with several portions of furnace slag did not result in a marked increase of uranium concentration in the extractants. Because of the inability to build up a sizeable uranium concentration in an extractant, as shown in the study of uranium distribution between furnace slag and bismuth, the success of a proposed high temperature extraction process seems unlikely.

The only solubilizing fusion treatment which resulted in any appreciable elimination of uranium from the slag was the one with calcium chloride. The uranium was not found concentrated in the magnetic material in the slag. None of the leaching agents tried extracted an appreciable amount of uranium from the slag. Cost calculations based on data obtained indicate that none of the treatments studied would result in an economic recovery process.

The data obtained for the solubility of uranium in antimony agree fairly well with similar data reported by Massachusetts Institute of Technology. The data obtained for the solubility of uranium in bismuth agree with values interpolated from the established binary phase diagram, but lie below the values reported by Massachusetts Institute of Technology, and above values reported by Brookhaven National Laboratory. The data obtained for the solubility of uranium in lead agree with values reported by the Massachusetts Institute of Technology, but lie below values interpolated from the established binary phase diagram. The data for the solubility of uranium in silver lie close to the reported solid solubility of uranium in silver, but lie well below the values reported by previous investigators. The data obtained for the solubility of uranium in tin agree with values reported by Massachusetts Institute of Technology, but lie below the values interpolated from the established binary phase diagram.

INTRODUCTION

Statement of Problem

Phosphate rock contains uranium in concentrations varying from 0.01 to 0.05 per cent depending on its source. Of the 11,095,204 long tons of phosphate rock used in the United States in 1951, 2,170,814 long tons or 20 per cent went into products derived from the electric furnace process for the production of phosphorus, such as phosphates, phosphoric acid, phosphorus and ferrophosphorus (21). Although electric furnace use of phosphate rock represents a minor fraction of the total rock used, it is estimated that the amount of uranium potentially recoverable from this source is about 300 tons per year. This estimate is arrived at in the following manner.

The potential phosphorus production in the United States is 310,000 tons per year (15). At 90 per cent conversion this would require 1,869,000 tons of calcium fluorapatite per year. If it is assumed that the average calcium fluorapatite content of all phosphate rock consumed for electric furnace use is 60 per cent, then 3,120,000 tons of rock would be consumed each year. If it is also assumed that all rock used for furnace feed is 0.01 per cent in uranium concentration, then approximately 300 tons of uranium is potentially recoverable from this source per year. This compares with the 1000 to 1500 tons of uranium potentially recoverable annually from the domestic production of superphosphate, again assuming that the phosphate rock used averages 0.01 per cent uranium.

In connection with the Atomic Energy Commission's program to exploit all possible domestic uranium resources, there has been much interest in the recovery of uranium from all of the phosphate rock mined in the United States. As an economic goal, thirty-five dollars per pound has been suggested as the upper limit for natural uranium for economical nuclear power production (3).

In the electric furnace process for the production of elemental phosphorus, phosphate rock, coke and silica are charged into the furnace. By the heat of the process, the following reaction is approximated, depending on the exact nature of the phosphate rock and proportions of rock, coke and silica used:

$$2\ Ca_{10}F_2(PO_4)_6 + 18\ SiO_2 + 30\ C$$

$$= 3\ P_4 + 30\ CO + 2\ CaF_2 + 18\ CaSiO_3.$$

The phosphorus and carbon monoxide leave the furnace as vapors. The CaF_2 and $CaSiO_3$ make up a slag, and the iron in the phosphate rock charge reacts with some of the phosphorus to make ferrophosphorus. These

materials are tapped off the bottom of the furnace as liquids. Figure 1 shows a typical flow diagram for the electric furnace process for the production of phosphorus and phosphoric acid. Figure 2 shows the cross-section view of an electric phosphate furnace.

A study at Battelle Memorial Institute (16) showed that the uranium in phosphate rock virtually all went into the slag when the rock was smelted in a Braun type assay furnace. In high temperature (2700°F.) reductions of phosphate rock, using an electric induction furnace and coke as the reducing agent, about 20 to 30 per cent of the uranium was volatilized, but most of the uranium went into the slags.

Uranium balances of a commercial scale electric furnace plant made by Virginia-Carolina Chemical Corporation (22) confirm the general conclusions derived from the Battelle data. It was found that from 26 to 77 per cent of the uranium in the phosphate rock went into the slag at the Charleston, South Carolina, furnace, and from 59 to 70 per cent of the uranium went into the slag at the Nichols, Florida, furnace. The remainder in both cases virtually all went into the furnace condenser water. It was concluded that the higher uranium concentration of the slags is a function of the lower uranium concentration of the phosphate rock used for these uranium balance studies.

Certain information concerning furnace slags in general is provided from data on furnace operations at Tennessee Valley Authority (19). The slag is tapped from the furnace at temperatures varying from 2650 to 2820°F. The slag is either transferred directly from the furnace into chill cars for disposal, or is granulated. Granulation at Tennessee Valley Authority consists of spraying the molten slag with a stream of water as it leaves the furnace. The slag-water mixture is then transferred to a reservoir, from which it is loaded into railroad cars for removal from the furnace site.

A typical Tennessee Valley Authority slag chemical analysis was as follows (in per cent): P_2O_5, 1.0; CaO, 50.0; SiO_2, 39.5; Fe_2O_3, 0.3; Al_2O_3, 6.2; F, 2.6; K_2O, 0.7; MgO, 0.3; MnO_2, 0.2; Na_2O, 0.6; S as SO_3, 0.2.

The only uses reported for slag are as a soil liming agent, and a road ballasting material. However, a number of other uses proposed are technically, although not economically, feasible. These include uses as a Portland cement constituent, slag wool, material for ceramic bodies and glazes and lightweight concrete blocks. The P_2O_5 content of the slag has some value as a fertilizer.

The exact nature of the uranium in these slags is not known. It has been postulated (23) that in phosphate rock the uranium is isomorphous

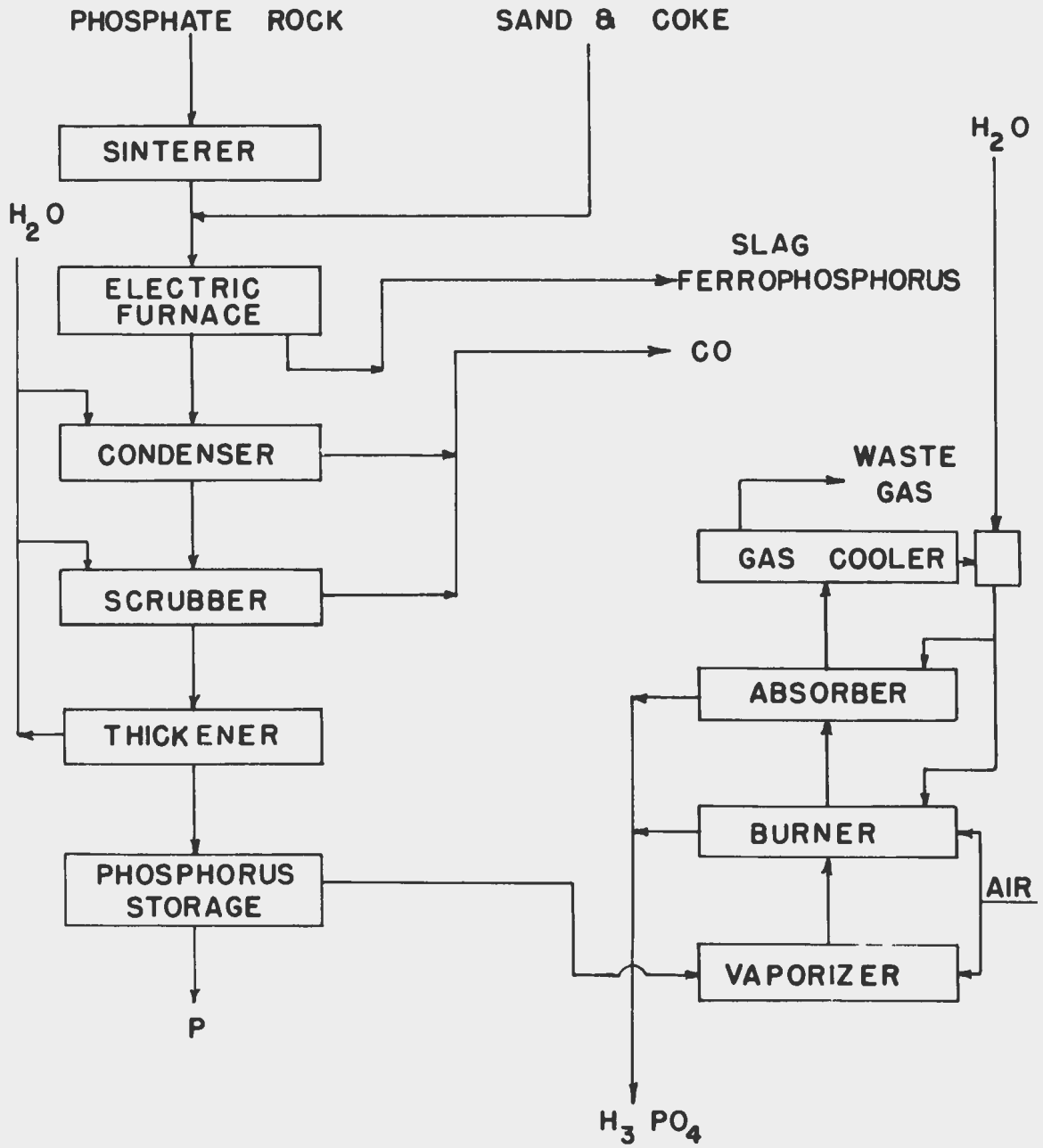

FIGURE 1. ELECTRIC FURNACE PROCESS FOR PHOSPHORUS AND PHOSPHORIC ACID. REPRODUCED FROM KOBE. "INORGANIC PROCESS INDUSTRIES." MACMILLAN. PAGE 326. 1948

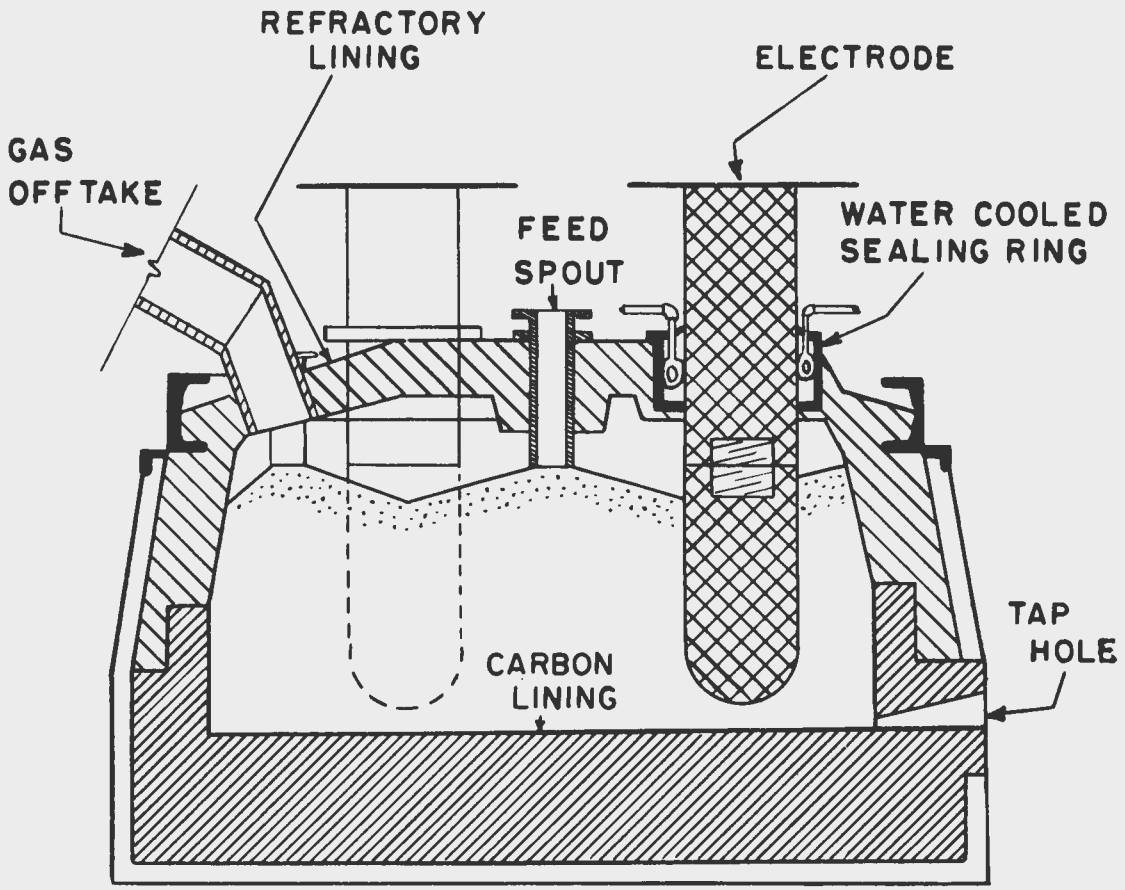

FIGURE 2. CROSS-SECTION VIEW OF ELECTRIC PHOSPHATE FURNACE. REPRODUCED FROM KOBE. "INORGANIC PROCESS INDUSTRIES," MACMILLAN. PAGE 327, 1948

with calcium. It seems probable that in furnace slags the uranium is still similarly associated with the CaO phase of the slag. Other possibilities are that intermetallic compounds of uranium are formed with iron or other metals, or that uranium oxides, carbides, phosphides, silicides, or sulfides are formed.

The problem of recovering most of the uranium from this fraction of the phosphate rock used resolves to one of developing some treatment of the furnace slag, which contains the bulk of the uranium from the furnace phosphate rock feed. The primary purpose of this investigation was to explore the possibility of economic uranium recovery from these slags.

As any uranium recovery treatment of the molten slag would eliminate the handling expense of the frozen slag, special emphasis was placed on the recovery of uranium from the slag by high temperature liquid-liquid extraction, using liquid metals as extractants. As an adjunct to this technique, the solubility of uranium in liquid metals was further studied.

The extremely low uranium concentrations in these materials made analytical procedures relatively important. A secondary purpose of the investigation was to develop radioassay and colorimetric methods of analysis for uranium in representative raw slags, and slag residues from experimental recovery treatments.

Previous Work on Recovery of Uranium from Slags

At Battelle Memorial Institute, a number of approaches were made to the recovery of uranium from the phosphate rock used in the electric furnace process (16). Additions of NaF to the melt, when phosphate rock was melted in a Braun type assay furnace, did not affect the uranium volatilization. Ferrophosphorus and ferrosilicon were ineffective as collectors or scavengers of the uranium from the slag produced in high temperature reductions of phosphate rock, using coke as the reducing agent. Chlorinations of the slags from these reductions resulted in about 15 per cent additional extractions, but this was proportional to the loss in weight of the slag during the treatment.

In other Battelle studies (5) an oxidizing roast was applied to the slags. Ten per cent of the uranium in the slag was eliminated by a four hour roast with 10 per cent sodium nitrate at 1652°F. However, the loss in weight of the slag was from 12 to 15 per cent of the charge. When a sample of this oxidized residue was further heated with 10 per cent NaF in a vacuum furnace at 1112° F. for four hours, no additional uranium removal resulted.

At Mound Laboratory, operated by the Monsanto Chemical Company, recovery of uranium from a slag from the Monsanto phosphorus furnace was

investigated (11). The slag contained 42.4 per cent CaO, 42.7 per cent SiO_2, and 9.7 per cent alumina, plus small amounts of phosphate, iron, sulfur, carbon dioxide, and sodium. The uranium concentration was about 0.006 per cent. Recovery treatments studied included leaching with various solutions, roasting with various chemicals, chlorination followed by water leaching, hydrothermal pressure treatments, fusion with various chemicals followed by water leaching, and complexing by organic phosphate. Of all these experiments, only acid leaching resulted in any appreciable uranium extraction. However, such a process would not be economically feasible, because the basic nature of the slag consumes a large amount of acid during the leaching process.

Tennessee Valley Authority (20) reports attempts to volatilize the uranium out of furnace slag by direct chlorination in the presence of carbon. In one run 6.0 grams of expanded slag analyzing 0.018 per cent uranium was mixed with 1.0 gram pine charcoal and directly chlorinated at 850°C. for three hours. The sublimate accounted for 44 per cent of the uranium input and the residue 58 per cent. In another run 6.0 grams of the raw slag was mixed with 1.0 gram of pine charcoal and chlorinated at 1000°C. for three hours. The sublimate analyzed 76 per cent of the uranium input and the residue 59 per cent. The residue from these chlorinations contained a considerable amount of water insoluble uranium. It was concluded that unless the uranium is volatilized as the chloride, this general method did not offer an easy means of uranium recovery from these slags.

Review of Literature on the Solubility of Uranium in Liquid Metals

The solubility of uranium in certain liquid metals was of interest in the high temperature uranium extraction studies. The purpose of this section is to present the criteria used to select certain systems for further study, present the techniques of previous investigators in this field, and compare their findings with data interpolated from established binary phase diagrams.

Considering all the metals in the periodic table (except the rare earths), boron, titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium and platinum are excluded as possible extractants for uranium in a high temperature extraction process, on the basis that their melting point lies above 1550°C. This temperature is considered to be an upper limit for such a process, based on the temperature at which the slags are tapped from the electric furnace.

Of the remaining metals, lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, radium, zinc, cadmium,

mercury, arsenic, antimony, selenium and tellurium are further excluded as possible extractants because their boiling point lies below 1400°C. Similarly, this temperature is considered the temperature below which such a process could not be operated, based on the melting point of the furnace slags.

As they would reduce the silica phase of the slag, beryllium, scandium, yttrium and aluminum of the remaining metals are excluded. This leaves copper, silver, gold, gallium, indium, thallium, silicon, germanium, tin, lead, bismuth, manganese, iron, cobalt and nickel as possible extractants on the basis of the above criteria. Of these metals, the binary phase diagrams for uranium and gold, gallium, indium, thallium, and germanium have not been established. They are excluded as possible extractants, however, because of their high cost and unavailability.

The binary phase diagrams for uranium and copper, silicon, manganese, iron, cobalt and nickel have been well established. On the basis of these facts, and certain other criteria, bismuth, silver, lead, tin, and antimony were selected for further study with regard to the solubility of uranium in them.

Lead, tin and bismuth have all been proposed as solvents for uranium in the liquid fuel reactor program. The U-Sn and U-Bi phase diagrams have been partially established, but the liquidus lines are still in doubt (12, p. 145, 121). The U-Pb phase diagram has recently been established, but the liquidus line is in doubt (13).

The U-Ag phase diagram has recently been established (4, p. 295), but the solubility of uranium in silver has been reported at several different values by various investigators. Silver has been proposed as a solvent for the pyrometallurgical purification of spent uranium from heterogeneous reactors. The U-Sb phase diagram has not been established, and antimony has been proposed as a solvent for uranium in the liquid fuel reactor program.

At Brookhaven National Laboratory, the solubility of uranium in liquid bismuth was studied in the range from 271 to 700°C. (2). In the settling technique employed by Brookhaven, the cleaned metals were transferred to a Pyrex or Vycor tube. The tube was partially evacuated by a mechanical vacuum pump until the metals were dry. The evacuation was then completed to 5×10^{-5} mm. Hg. at room temperature. The glass tube was heated to about 250°C. by a small wire-wound alundum tube furnace which fitted around the glass tube. The metals were sealed off in the glass tube and held overnight at 400°C. to allow formation of UBi_2. The capsule was then cooled, and set aside for use in a constant temperature settling furnace.

The solubility of uranium in bismuth was determined by holding the U-Bi alloy mixture at a constant temperature for a period long enough to allow the UBi_2 to settle to the bottom of the melt, and allow equilibrium to establish between the UBi_2 and uranium in the liquid phase of the melt. The capsule described above was centered in a stainless steel tube, and graphite packed around it. The steel tube was put into a wire-wound alundum muffle furnace. Santocel insulation was put over the steel tube. The furnace was turned on and controlled at the desired point. At the end of the settling time, the sample was quenched by almost covering the steel tube in ice water. The capsule was removed from the steel tube for analysis.

In the filtering technique employed by Brookhaven, the cleaned metals were placed in a coarse Pyrex filter tube, and the tube evacuated as in the settling procedure. The tube was heated by a wire-wound silica tube furnace, which fitted around the tube, and the vacuum held at 5×10^{-5} mm. Hg. The temperature was maintained at 400°C. overnight to allow the metals to form UBi_2 in excess of that which is liquid at the equilibrium temperature. The melt was then held at the desired temperature at least one-half hour. Argon gas was used to force the liquid through the filter. The filter tube was then evacuated and cooled. All chemical analyses for these data were performed using a polarographic procedure.

Hayes and Gordon have reported the solubility of uranium in several metals and alloys (8, p. 130). The general technique used was to heat the alloy to a temperature in the single phase region, cool to some temperature below this and hold for a period of several hours. A sample of the liquid in the alloy at this temperature was then withdrawn for chemical analysis. The alloy was cooled to a lower temperature, allowed to soak, sampled, and this process repeated at several temperatures down to the point of solidification.

The furnace used consisted of a resistance wound alundum muffle, around which were packed several inches of insulation. Stainless steel tubes through the brass furnace top allowed accesses for the protective atmosphere, thermocouple, motor driven stirring rod, and sampling tube. Beryllia lined alundum crucibles large enough to give a melt 4 inches deep and 1 3/4 inches in diameter were used for most alloys. Argon was used as a protective cover for most of the alloys. The uranium metal was added as well as sampling done through the stainless steel sampling tube. The thermocouple was protected chromel-alumel. The stirring rod was fashioned by cementing alundum paddles to a 3/16 inch alundum rod and firing the assembly with a slip coat of beryllia.

In making a run, the uranium, after careful cleaning and oxide removal, was quickly added to the melt through the sampling tube. In this way oxidation was kept at a minimum. The sampling was accomplished

by vacuum sucking the molten metal up into a Pyrex glass tube inserted about 1/4 inch below the surface of the liquid. A thick-walled capillary upper section of the tube served to freeze the metal as it was drawn up, and a constriction at the lower end helped to hold the sample in the tube until it solidified. A check on equilibrium conditions was made by making reruns of the melts and comparing results against each other.

For purposes of comparison, Table 1 presents a summary of data from three sources for the solubility of uranium in four of the five metals chosen for study. All values are reported as grams of uranium per 100 grams of the solvent metal.

Data on the solubility of uranium in silver are reported by a number of investigators. Workers at Ames Laboratory report the data presented in Table 2 (6, p. 34). High purity silver was contacted with pure uranium at 1200°C., in either beryllium oxide, tantalum, or zirconium dioxide crucibles, using induction heating. The alloy was then equilibrated at the desired temperature to allow separation of the phases. The National Bureau of Standards reports the solid solubility of uranium in silver to be between 0.1 and 0.4 weight per cent from 25°C. to 950°C. and a eutectic occurring at 950°C. and approximately 5 per cent uranium (4, p. 300).

From the above discussion, it is clear that data on the solubility of uranium in liquid metals are scanty, and that the data obtained using the procedures described do not agree with the established phase diagrams in certain cases.

MATERIALS AND APPARATUS

Materials

Four samples of representative electric furnace phosphorus slag were obtained for experimental purposes. Two of the slags were from the Westvaco Chemical Division of the Food Machinery and Chemical Corporation at Pocatello, Idaho. The first sample was obtained in 1951, and the second sample in 1954. One sample of slag was obtained each from the Virginia-Carolina Chemical Company at Charleston, South Carolina, and the Monsanto Chemical Company at Columbia, Tennessee. Table 3 summarizes the source of these slags, and the condition in which they were received.

To prepare the slags for characterization of their components, their size was reduced by a crushing operation, consisting of consecutive passes through a jaw crusher, a roll crusher and a disc pulverizer. Table 4 presents a typical screen analysis of the products obtained from these

Table 1

Comparison of Several Values of Solubility of Uranium in Sb, Bi, Pb and Sn. Values Expressed as Grams Uranium per 100 Grams Solvent Metal.

Temperature °C.	Bismuth			Tin		Lead		Antimony
	BNL	MIT	NNES Phase Diagram	MIT	NNES Phase Diagram	MIT	Maskrey and Frost Phase Diagram	MIT
1000	-	-	-	-	10.6	-	4.0	-
950	-	-	27.1	-	9.7	-	3.5	-
900	-	16.0	15.5	-	8.1	0.6	2.9	3.0
850	-	11.7	11.4	0.4	6.4	-	2.7	1.8
800	-	8.7	7.8	-	5.6	-	2.1	0.8
750	-	6.4	5.7	0.06	4.7	-	1.9	0.5
700	3.1	5.0	4.3	-	3.9	0.06	1.6	0.3
650	2.1	3.6	2.8	-	3.1	-	1.6	0.2
600	1.5	2.6	2.3	-	2.3	-	1.6	-
550	1.0	1.8	1.9	-	2.0	-	1.1	-
500	0.6	1.0	1.4	-	1.5	0.02	1.1	-
450	0.4	-	1.2	-	1.2	-	1.1	-
400	0.2	-	0.9	-	0.8	-	1.1	-
350	0.1	-	0.7	-	0.6	-	0.7	-
300	0.1	-	0.5	-	0.4	-	-	-

Table 2

Ames Laboratory Data for Solubility of Uranium in Silver

T., °C.	Time-hr.	Crucible	Weight Per Cent U in Silver Phase
1240	3/4	ZrO_2	4.00
1190	1/2	Ta	4.75
1135	10	BeO	3.88

Table 3

Source and Condition as Received of Electric Furnace Slags

Slag	Source of Slag	Source of Furnace Feed Rock	Condition as Received
Westvaco No. 1	Westvaco Chemical Division Food Mach. and Chem. Co. Pocatello, Idaho	Idaho deposits	Coarse lumps
Westvaco No. 2	Westvaco Chemical Division Food Mach. and Chem. Co. Pocatello, Idaho	Idaho deposits	Coarse lumps
Virginia-Carolina	Virginia-Carolina Chem. Co. Charleston, South Carolina	Florida deposits	Small lumps
Monsanto	Monsanto Chem. Co. Columbia, Tennessee	Florida or Tennessee deposits	Granular

Table 4

Typical Screen Analysis of Crushed Westvaco Furnace Slag, with Radioassay Count of Each Fraction

Tyler Std. Screen Mesh Retaining	Per Cent Retained	Radioassay C/M over BG
48	0.8	-
65	3.3	64.6
100	14.4	61.5
150	18.3	56.8
200	19.7	59.5
270	18.0	59.5
< 270	25.5	59.9
	100.0	

operations, with the radioassay count of each fraction.[1] This latter value is expressed as counts per minute over the prevailing background count.

Samples of three of the slags were analyzed for the primary slag constituents. In addition the slags were analyzed for P_2O_5 using the AOAC procedure for total P_2O_5 analysis (1). Table 5 summarizes these analyses.

The slags were analyzed qualitatively for the minor slag constituents using spectrographic procedures. These data are tabulated in Table 6.

The radioassay and colorimetric analysis of the slags for uranium are discussed in the Appendix. Table 7 summarizes the analysis of the raw slags for uranium, with a comparison of three methods. Since the Westvaco slag was used for most of the exploratory experiments most of the analytical work was done on it.

[1] See Appendix.

Table 5

Chemical Analyses for Major Slag Constituents

Constituent	Composition of Slag, Per Cent		
	Westvaco No. 1	Virginia-Carolina	Monsanto
CaO	45.9	54.6	45.8
SiO_2	51.9	43.0	41.1
Al_2O_3	2.0	2.4	2.7
Fe_2O_3	0.8	0.3	0.3
MgO	1.2	0.7	0.6
P_2O_5	3.6	2.1	0.8
F-[a]			

[a]Estimated at between 1.0 and 2.0 per cent for each slag.

Table 6

Spectrographic Analyses of Minor Slag Constituents

Element	Qualitative Spectrographic Analysis, Per Cent			
	Westvaco-1	Westvaco-2	Virginia-Carolina	Monsanto
Boron	< 0.01	< 0.01	-	< 0.01
Barium	> 1.0	0.01 - 1.0	> 1.0	> 1.0
Chromium	0.01 - 1.0	0.01 - 1.0	< 0.01	< 0.01
Copper	< 0.01	< 0.01	< 0.01	< 0.01
Manganese	0.01 - 1.0	0.01 - 1.0	0.01 - 1.0	0.01 - 1.0
Nickel	< 0.01	< 0.01	< 0.01	< 0.01
Silver	< 0.01	< 0.01	< 0.01	< 0.01
Strontium	> 1.0	0.01 - 1.0	> 1.0	> 1.0
Titanium	< 0.01	< 0.01	< 0.01	< 0.01
Vanadium	< 0.01	< 0.01	< 0.01	< 0.01
Yttrium	< 0.01	< 0.01	< 0.01	< 0.01
Zirconium	-	-	-	< 0.01

Table 7

Uranium Analyses of Four Electric Furnace Slags

Slag	Radioassay Method	Colorimetric Method #1	Colorimetric Method #2
Westvaco #1	0.0098%[a]	0.0120%[c]	0.0101%[d]
Westvaco #2	0.0105%[b]	-	0.0111%[e]
Virginia-Carolina	0.0048%[b]	0.0066%[c]	0.0058%[e]
Monsanto	0.0069%[b]	-	0.0059%[e]

[a]Represents the average of 53 counts.

[b]Represents the average of 8 counts.

[c]Represents the average of 4 replicate analyses, using the Rodden method for the analysis of uranium in phosphate rock.

[d]Represents the average of 30 replicate analyses, using the modified Rodden procedure for the analysis of uranium in furnace slags.

[e]Represents the average of 10 replicate analyses, using the modified Rodden procedure for analysis of uranium in furnace slags.

The materials used in this study include a wide variety of metals and compounds. CP grade reagents were used in each case.

Apparatus

Figure 3 shows the details of a small Globar resistance furnace and its auxiliary equipment. The furnace and rheostat were purchased as a unit from The Sentry Company, Foxboro, Massachusetts. The furnace consisted essentially of an elliptical steel shell, 14 inches along the

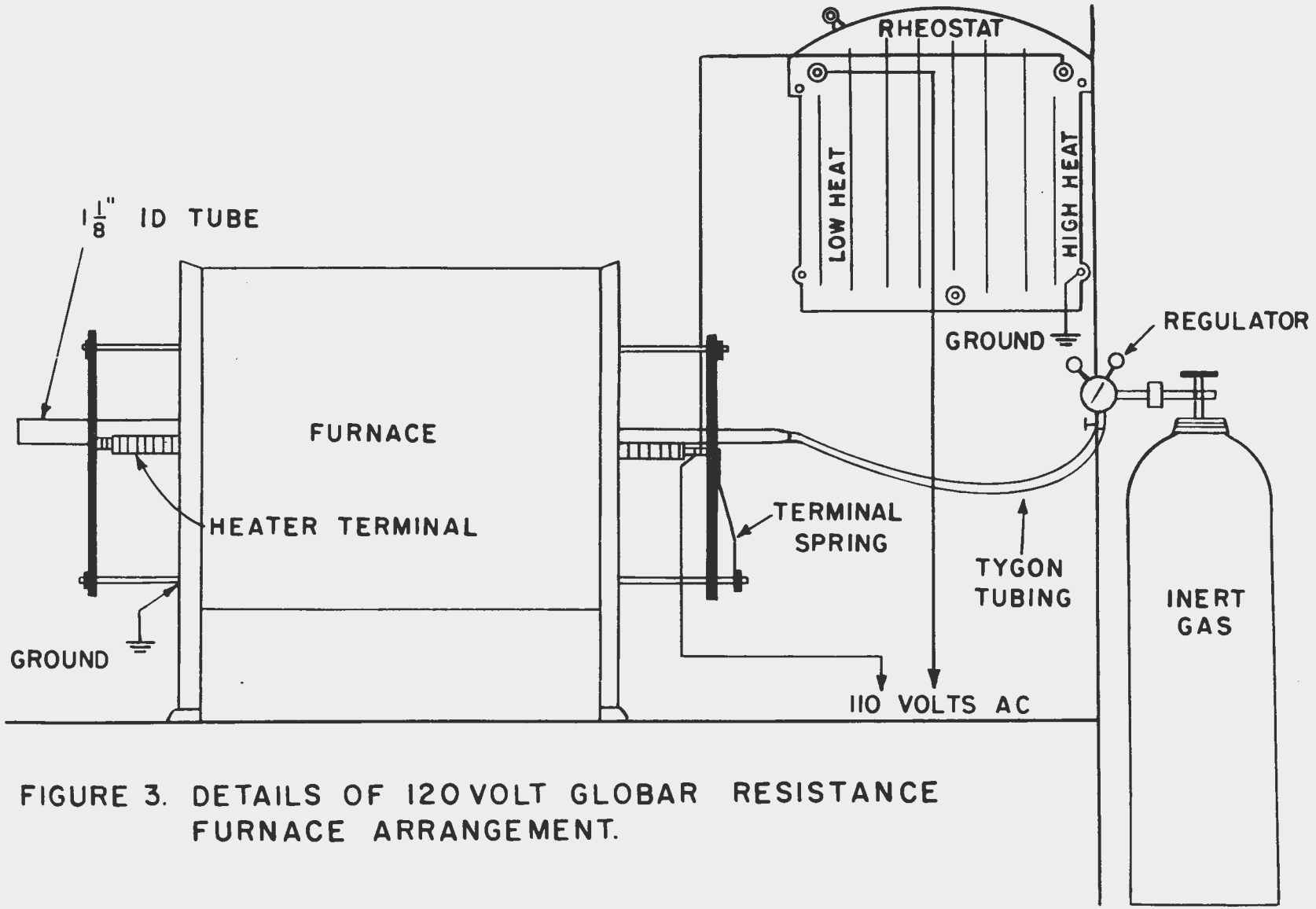

FIGURE 3. DETAILS OF 120 VOLT GLOBAR RESISTANCE FURNACE ARRANGEMENT.

major axis, and 20 inches long. The shell enclosed approximately 4 inches of insulation at the top and bottom, and 6 inches of insulation at the sides. A hearth in the furnace allowed room for the two Globar heating elements, and the refractory tube. The two silicon carbide Globar heating units were held in place as shown by the heater terminals, and the proper tension on the Globar rods for good electrical contact supplied by the terminal spring at one end of the furnace. The Sillimanite tube was 26 inches long, and was necked down at one end to allow easy input of the desired atmosphere to the tube.

This furnace was rated at 1400°C. maximum temperature, and was operated satisfactorily at this temperature, over sustained periods of time. The rheostat provided control of temperature over a wide range. Although a thermocouple hole was provided in the furnace, continued thermocouple failure made it necessary to measure temperatures with an optical pyrometer.

The sample size in this furnace was limited to 30 grams. Virtually no mixing was achieved. Another disadvantage was that the Globar resistors increased in electrical resistivity with age, making it increasingly time-consuming to attain the desired temperature.

For the solubilizing fusion experiments, a small gas-fired furnace was constructed. Figure 4 shows details of this furnace. The furnace was made of 14 No. K-28 insulating firebrick. Eight of the bricks were cut out to give a 5 inch diameter cylindrical hearth, 8 inches high. The top two bricks were also cut-out to give a 1 inch sight hole for temperature readings. A 2 inch ID alundum tube, 4 inches long, served as the crucible support, and was placed on top of the second layer of brick. Heat was initially supplied to the alundum ring by ignition of a gas-air mixture in the two torches. When the surface of the alundum was at red heat, the gas flow was increased enough to extinguish the torch flame, but allow combustion of the gas-air mixture in the hot combustion chamber.

It was possible to heat 50 grams of material to temperatures of about 2350°F. for sustained periods of time. Temperatures were read directly off the crucible by sighting the optical pyrometer into the mirror over the sight hole. This furnace was limited in both temperature and capacity, but some mixing was probably achieved by thermal convection, due to the temperature difference between the top and bottom of the crucible.

Figure 5 shows the details of a larger Globar resistance furnace similar to the small furnace described. The details of this furnace are essentially the same as for the smaller furnace, except for size and mode of temperature control. The furnace was an elliptical steel shell, 16 inches across the major axis, and 16 inches long. There is a hearth large enough to contain a 3 inch OD bore refractory tube, with 4 silicon carbide heating elements parallel to the tube. However, it was found

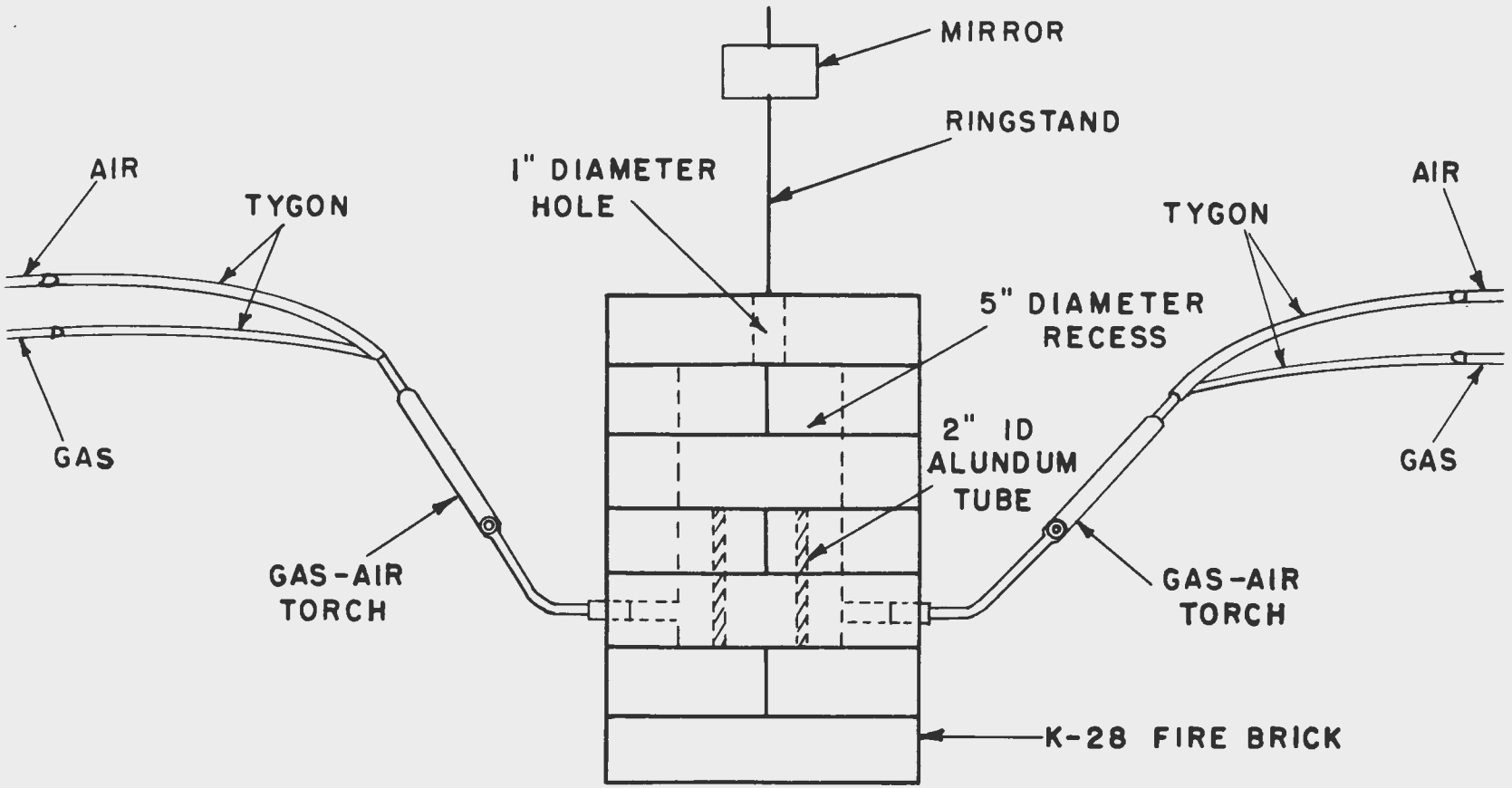

FIGURE 4. DETAILS OF GAS-FIRED FURNACE USED FOR SOLUBILIZING FUSIONS.

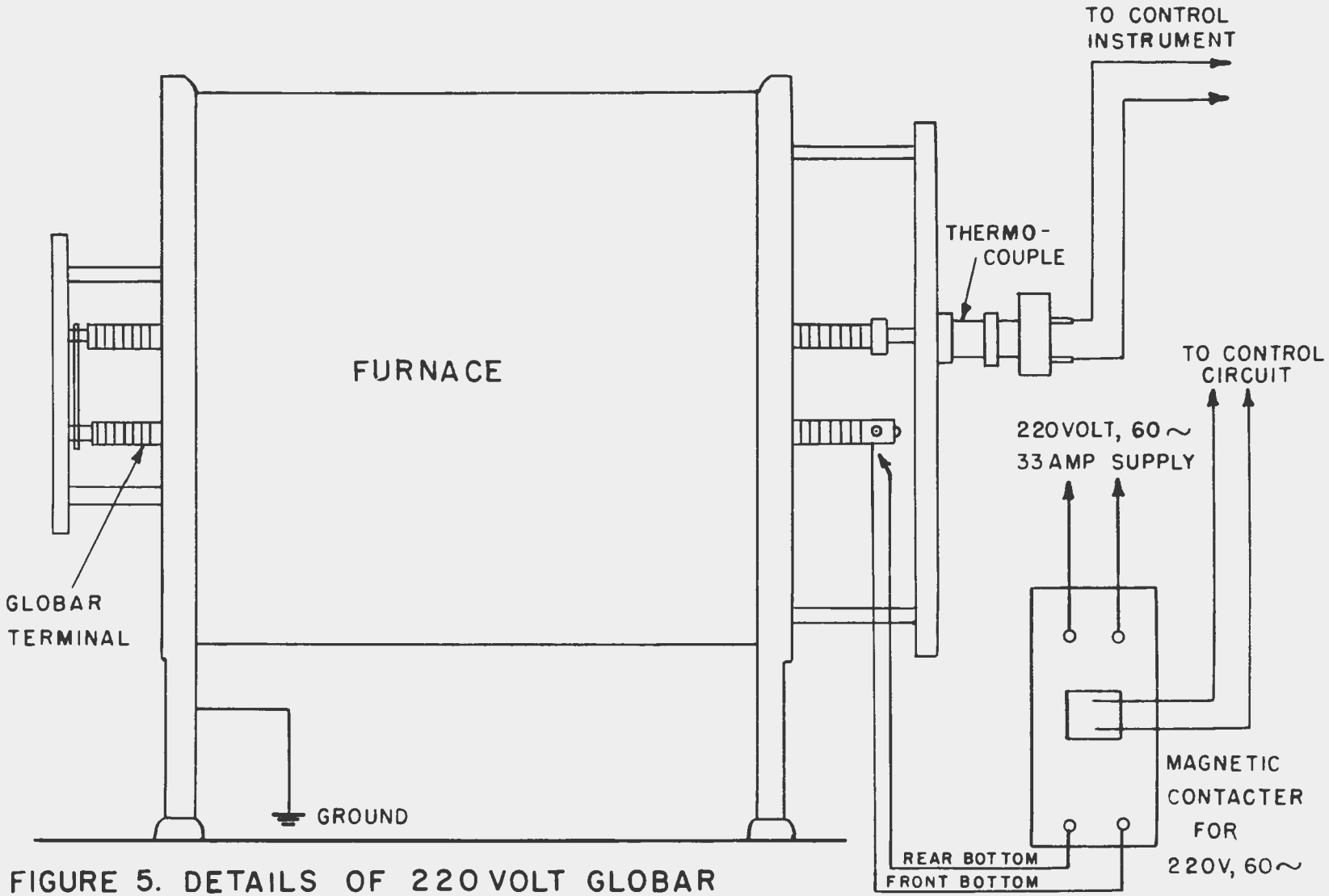

FIGURE 5. DETAILS OF 220 VOLT GLOBAR RESISTANCE FURNACE.

more feasible to use this furnace without the tube. It was possible to heat up to 250 grams of material to 2750°F. for sustained periods of time, or 2850°F. for a short period of time. An inert atmosphere was provided by sealing one end of the furnace with transite and refractory cement, except for a 1/4 inch gas inlet in the transite.

The temperature was controlled by means of a protected platinum-rhodium thermocouple, placed at the roof of the furnace, in conjunction with a Brown Pyr-O-Vane temperature controller. The setting of the controller for the desired temperature allowed control of temperature to within 15°F. of the setting. The controller operated by feed-back through the magnetic contactor, which controlled the 220 volt input to the furnace. With this furnace, it was possible to periodically rock the crucible during the melting period, thus mixing the melt somewhat.

For the investigation of the solubility of uranium in liquid metals, it was necessary to have a furnace in which the temperature could be controlled to within a few degrees at temperatures from 300 to 1100°C. Thus a resistance-wound furnace was constructed. The details of this furnace are shown in Figure 6. The Kanthal A resistance wire was wound on the middle 10 inches of the alundum tube and three coats of No. 7 Saureisen cement applied to the wound section. After the cement was baked for 24 hours at 115°F., the tube was fitted in the 1/4 inch recess of the bottom transite circle. The galvanized steel sheet was put into the groove in the transite, and the annular space around the tube filled with Dicalite insulation. The lead wires were attached to the two brass bolts in the cover, and the cover placed on the furnace. The assembly was completed by putting nuts on the threaded steel tie rods, which held the furnace together. The furnace was operated by a 115 volt variac, and drew 10 amperes at 115 volts. To bring the crucibles into the hot zone of the furnace, circles of insulating firebrick were cut, and placed in the alundum tube to a height of 7 1/2 inches. Mixing was attained by use of a graphite stirring impeller.

Figure 7 presents the details of an induction furnace setup used for some of the investigation. The converter drives the water-cooled primary induction coil from a 220 volt line source. Figure 8 shows details of the heater, which fits inside of the primary coil. This heater contains the graphite liner which serves as the secondary of the furnace circuit. The currents induced in this by the primary cause power dissipation in the secondary, and give the heating effect.

With this furnace it was possible to attain over 2000°C. for sustained periods of time. The heating rate was fast. The eddy current and hysteresis effects in the secondary gave a mixing effect which was very desirable where equilibrium between two phases was to be established rapidly. For some experiments, impeller mixing was added to this furnace,

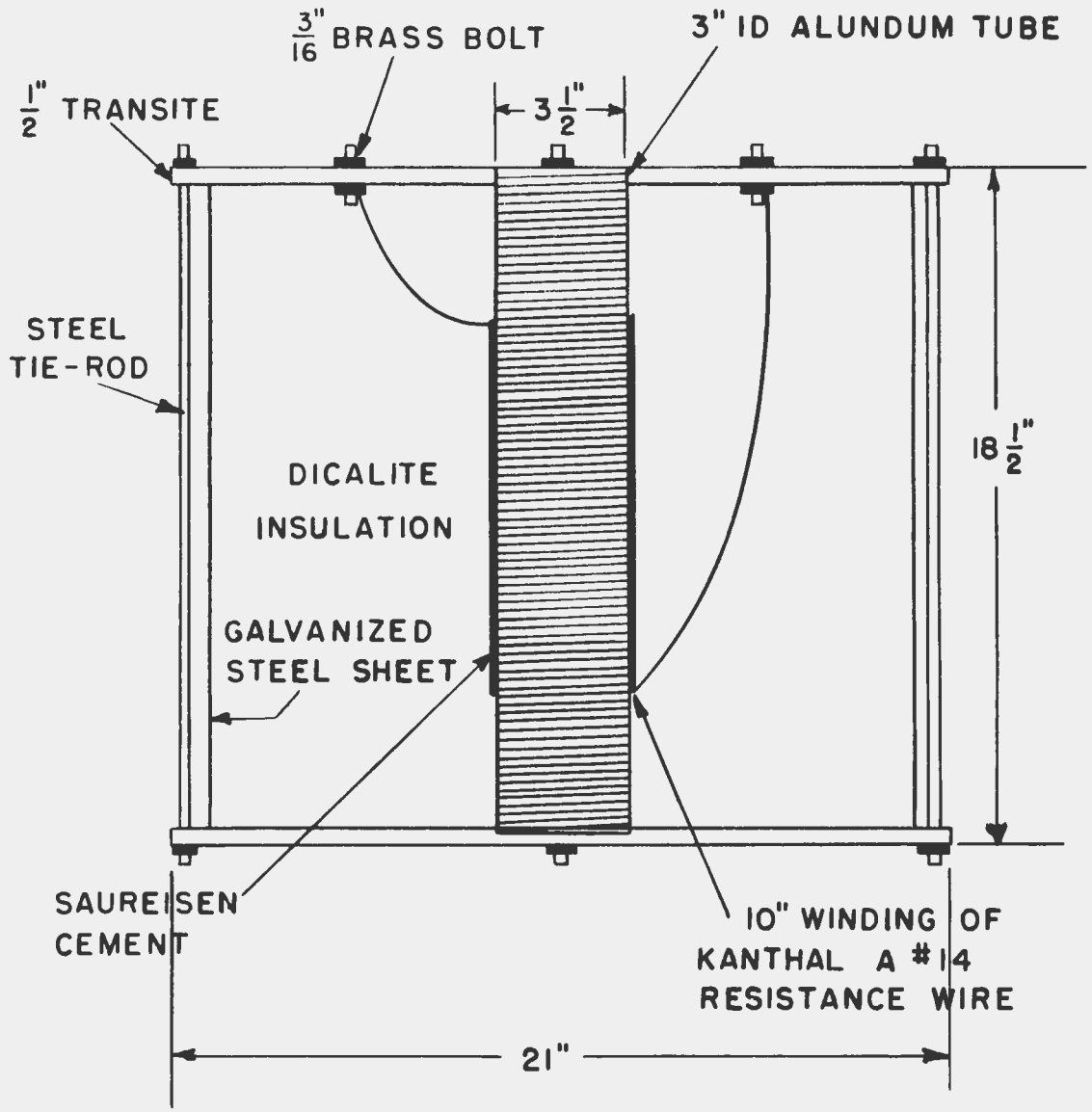

FIGURE 6. DETAILS OF WIRE-WOUND RESISTANCE FURNACE

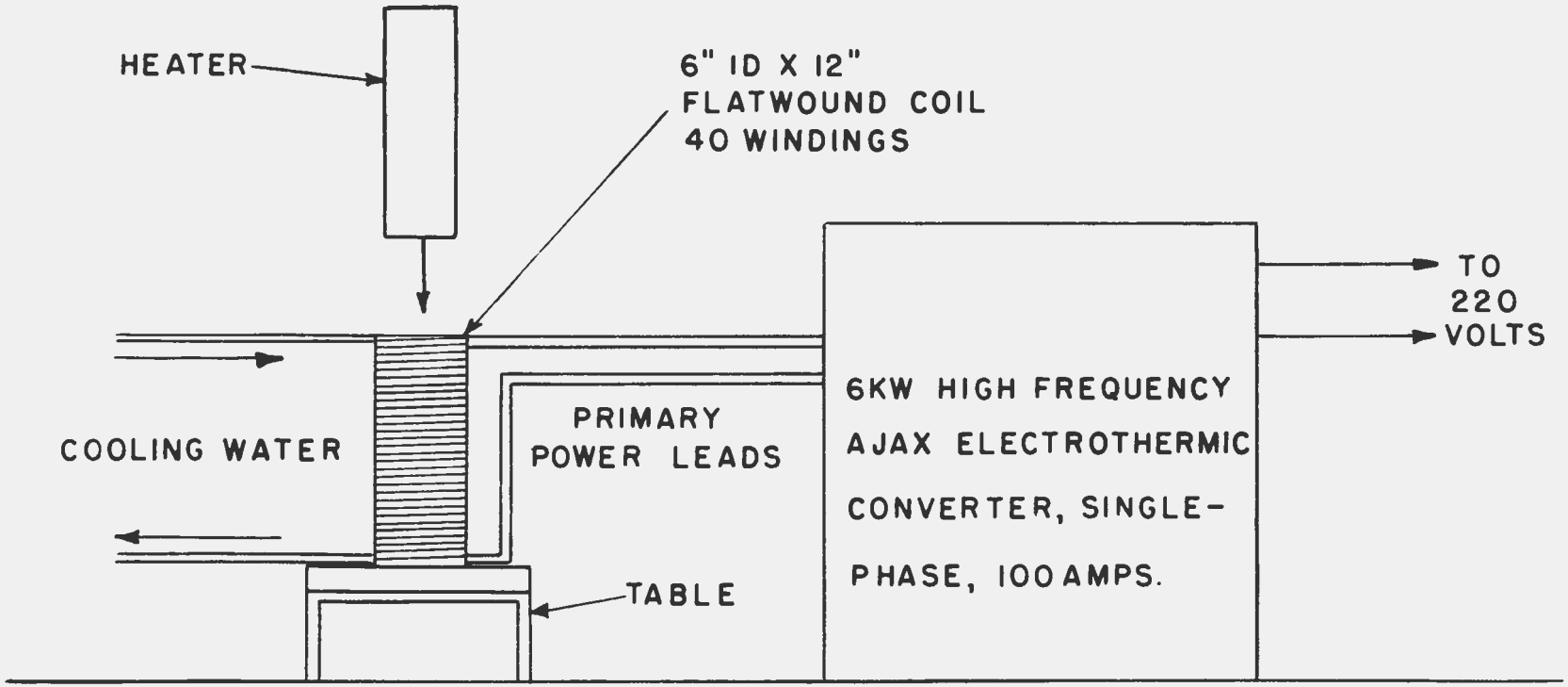

FIGURE 7. DETAILS OF HIGH-FREQUENCY INDUCTION FURNACE.

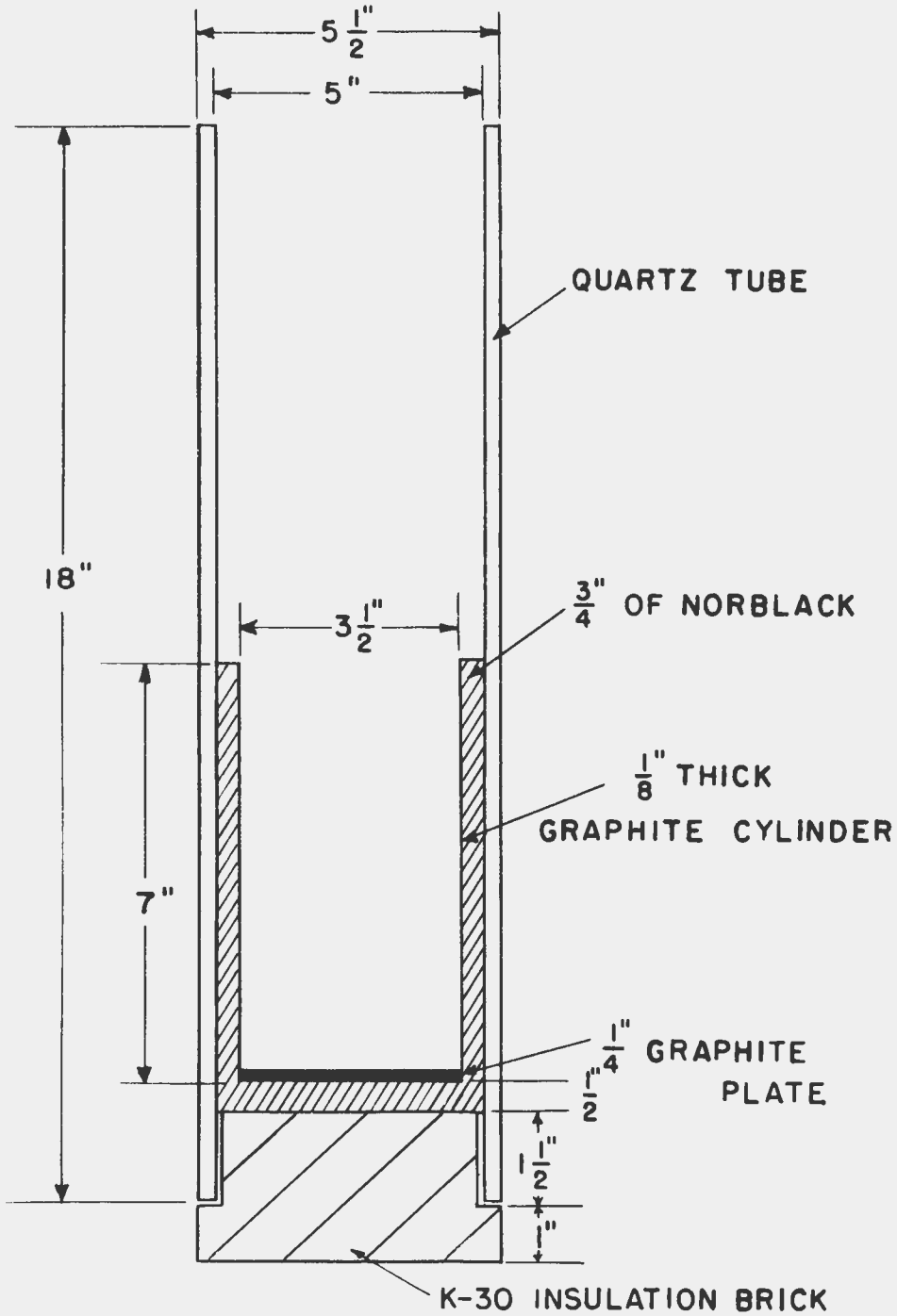

FIGURE 8. DETAILS OF INDUCTION FURNACE HEATER

for even better agitation of the melt.

EXPERIMENTAL STUDIES

General Procedures

The Westvaco slag analyzing 0.0098 per cent uranium by radioassay was used for all experiments on the recovery of uranium from furnace slags. In some experiments premixing of the slag and extractant was performed by tumbling the materials in a sample jar. The jar was fastened to the speed reduction gear of a laboratory stirring motor.

All crucibles used for the high temperature experiments were fabricated of National Carbon grade AGX graphite, in the Graphite Shop of Ames Laboratory. In general, the crucibles used in the small Globar furnace were 7 inches long, 13/16 inches deep, and 5/8 inches wide, inside dimensions. The crucibles used in the large Globar furnace were 6 inches long, 3/4 inches deep and 1 1/4 inches wide, inside dimensions. The crucibles used in the induction furnace and wire-wound resistance furnace were cylindrical, 6 inches total height, and 3 inches outside diameter. Special modifications and additions to these basic crucibles are described in connection with specific experiments to which they apply.

For all high temperature experiments except the solubilizing fusion treatments, a stream of argon or helium was passed over the melt at all times. All temperature measurements for the experiments on uranium recovery from furnace slag were made with a Model 8622 Leeds and Northrup optical pyrometer.

All residues from experimental treatments were pulverized in an iron mortar and pestle, and radioassayed according to the procedure described in the Appendix. In some cases the extractant phase was also radioassayed, not for absolute uranium content, but as an indication of uranium pick-up by the extractant. In a fraction of the cases, the radioassay value was checked by the colorimetric analysis procedure described in the Appendix. For both radioassay and colorimetric analysis results, the per cent uranium recovery or elimination was calculated as:

$$\text{Per cent uranium recovery or elimination} = \frac{\text{Initial per cent uranium} - \text{Final per cent uranium}}{\text{Initial per cent uranium}} \times 100.$$

The initial per cent uranium values are those presented in Table 7.

Thermal Reduction with Alkaline Earth Metals

By consideration of Figure 1, it appears feasible to recover the uranium from the slag when it is tapped from the furnace in a molten condition. Katz and Rabinowitch state that calcium, magnesium, and aluminum will reduce UO_2, U_3O_8 and UF_4 to uranium metal (9, p. 127). It was postulated that these metals would reduce the uranium out of the slag. The reductant would be mixed continuously with the molten slag as it is tapped from the furnace. The treated molten slag would be held in a settling reservoir to allow the reduced uranium to settle to the bottom of the melt, and then dumped according to the usual practice.

To simulate this proposed recovery process the following experiments were performed. Various amounts of calcium and magnesium metal were mixed with about 30 grams of the crushed slag for 30 minutes. The mixture was placed in a graphite crucible and heated to 2500°F. in the small Globar furnace. The melt was held at this temperature for 15 minutes. After the melt had cooled, it was partitioned into a top and bottom layer, using a carborundum cutting wheel. Each of the layers were pulverized to -100 mesh, and radioassayed. Graphite shavings from the boats were also radioassayed in some cases, to see if the graphite had adsorbed any of the uranium. The results of these reductions are summarized in Table 8.

The results of the thermal reduction experiments do not indicate a concentration of uranium in either layer of the partitioned slag residues. Increasing the amount of reducing agent has no effect on the disposition of uranium in the melt. The graphite does not adsorb any of the uranium from the melt.

In these experiments it was difficult to obtain a good partition of the small amount of slag residue. The inability to obtain a partition of the uranium may also be related to the short settling time of 15 minutes, which was not varied in the experiments.

Solubility of Uranium in Liquid Metals

As an adjunct to the high temperature liquid-liquid extraction of uranium from molten electric furnace slags, the solubility of uranium in liquid antimony, bismuth, lead, silver and tin was determined. All of these data were obtained using the crucible arrangement shown in Figure 9, in conjunction with the wire wound resistance furnace.

The uranium metal used was in the form of turnings. The oxide film was removed from the metal in 1 to 2 nitric acid. The cleaned metal was rinsed in absolute alcohol, and dried on absorbent paper. The metal for

Table 8

Data for Thermal Reduction Experiments

	Charge				Top Layer				Melt Graphite		Bottom Layer			
Reductant	Weight of Reductant Grams	Grams Slag	Per Cent Reductant	Premixing Time - min.	Weight Grams	Radioassay Count	Per Cent Uranium	Colorimetric Analysis Per Cent	Weight Grams	Count	Weight Grams	Radioassay Count	Per Cent Uranium	Colorimetric Analysis Per Cent
Calcium	0.8	39.2	2.0	30	5.74	61.8	0.0108	0.0067	4.73	11.6	9.04	58.4	0.0102	0.0088
Calcium	1.2	28.8	4.0	30	7.56	53.6	0.0093	0.0066	3.38	1.2	9.31	52.3	0.0091	0.0087
Calcium	1.8	28.2	6.0	30	9.30	51.0	0.0089	0.0102	2.98	1.4	6.75	45.7	0.0080	0.0038
Calcium	2.4	27.6	8.0	30	9.47	49.3	0.0086	0.0292	3.18	1.4	8.78	47.8	0.0083	0.0063
Calcium	3.0	27.0	10.0	30	8.54	47.7	0.0083	0.0207	-	-	8.16	41.2	0.0072	0.0225
Magnesium	0.6	28.4	2.0	30	6.81	58.1	0.0101		-	-	5.51	54.5	0.0095	
Magnesium	1.2	28.8	4.0	30	8.53	52.1	0.0091	0.0073	-	-	6.88	50.0	0.0087	0.0096

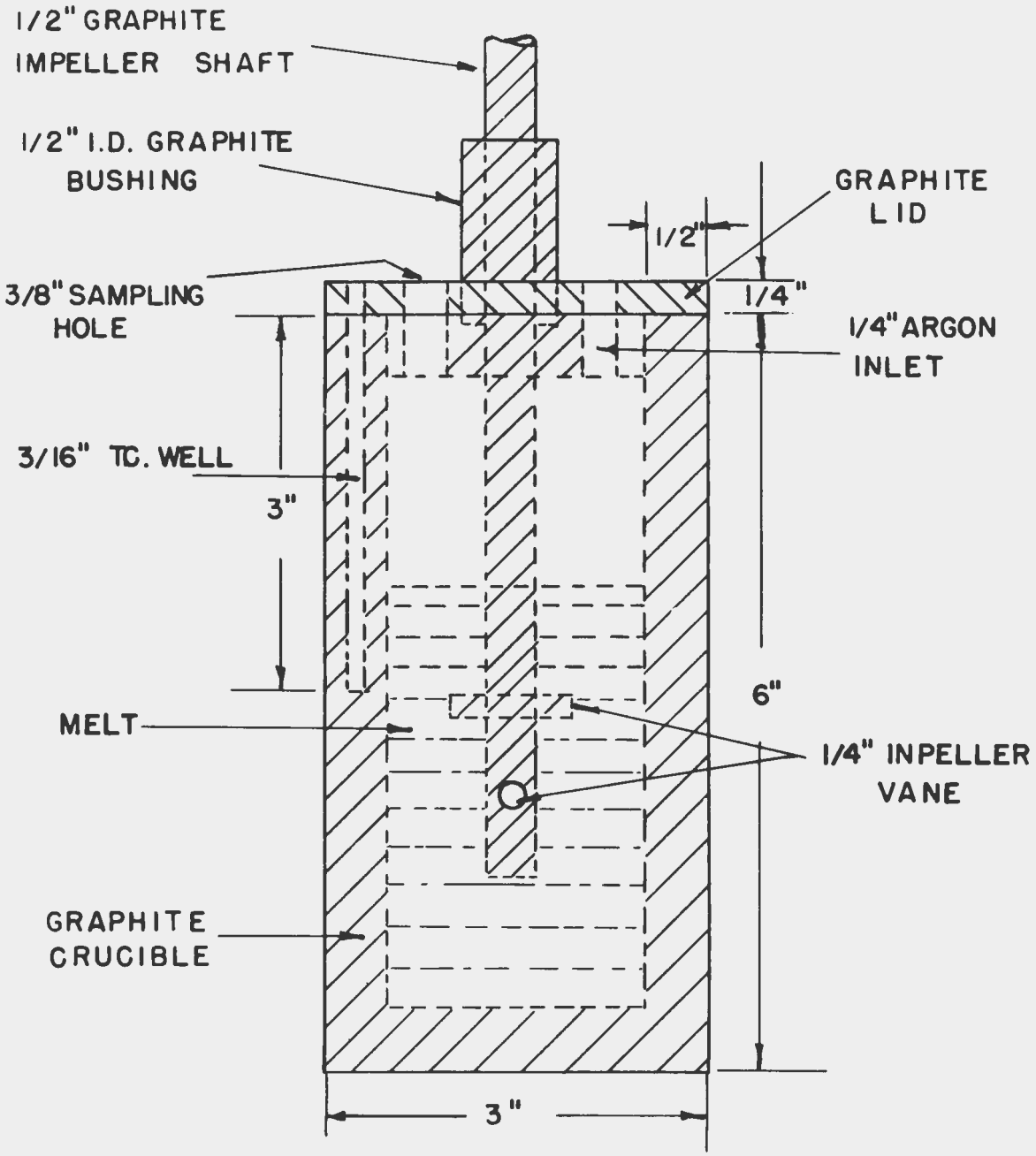

FIGURE 9. DETAILS OF WIRE-WOUND RESISTANCE FURNACE CRUCIBLES

each run was cleaned immediately prior to each run.

The amounts of the metals for each solubility determination were calculated to give a melt between two and three inches in depth. The metals were put into the crucible, and the furnace assembly completed with the graphite lid and stirring impeller. Circles of transite were cut, drilled and placed over the entire crucible assembly to the height of four inches. A piece of stainless steel tubing was used to pass the argon through the graphite lid over the melt. The connection between the argon tank and the tubing was made by means of tygon tubing. A graphite plug was placed over the sampling access, except when a sample was being taken.

Before the furnace was turned on, argon gas was passed over the melt for a period of twenty minutes. The melt was then heated rapidly to a temperature just above the highest temperature of interest. The melt was stirred for three hours at this temperature, using the graphite stirring impeller. The impeller was driven by a laboratory stirring motor. All temperatures were measured by means of a chromel-alumel thermocouple inserted into the well provided in the crucible wall, in conjunction with a Leeds-Northrup potentiometer.

At the end of the stirring period, the temperature was lowered to the desired temperature, and held at this temperature for a period of 1 1/2 to 2 hours. Samples were taken of the liquid phase every one-half hour during the settling period. Sampling was accomplished by means of the sampler shown in Figure 10. The weir opening was inserted to a distance of approximately one-half inch below the surface of the melt. The sample was quenched in argon as it was withdrawn from the melt.

The cycle of cooling, settling and sampling was repeated at several temperatures above the solidification temperature of the melt. The samples obtained were analyzed using the methods described in the Appendix.

Solubility of Uranium in Antimony

From Table 9 it is apparent that at 953.7°C. and 846.4°C. the excess uranium in the melt has settled out of the melt within 30 minutes. At 753°C., the viscosity of the cooler melt apparently inhibited the settling rate. It is nevertheless thought that the value at 90 minutes represents the solubility of uranium in antimony at this temperature. The per cent uranium values at 90 minutes settling time are plotted versus temperature in Figure 11. The values reported by Hayes and Gordon are also plotted for purposes of comparison. The data obtained are seen to give virtually a straight line temperature-solubility relationship, but with a lesser slope than the comparative data. The solubility at 953.7°C. could indicate insufficient mixing during the solvent saturation period, or a break in

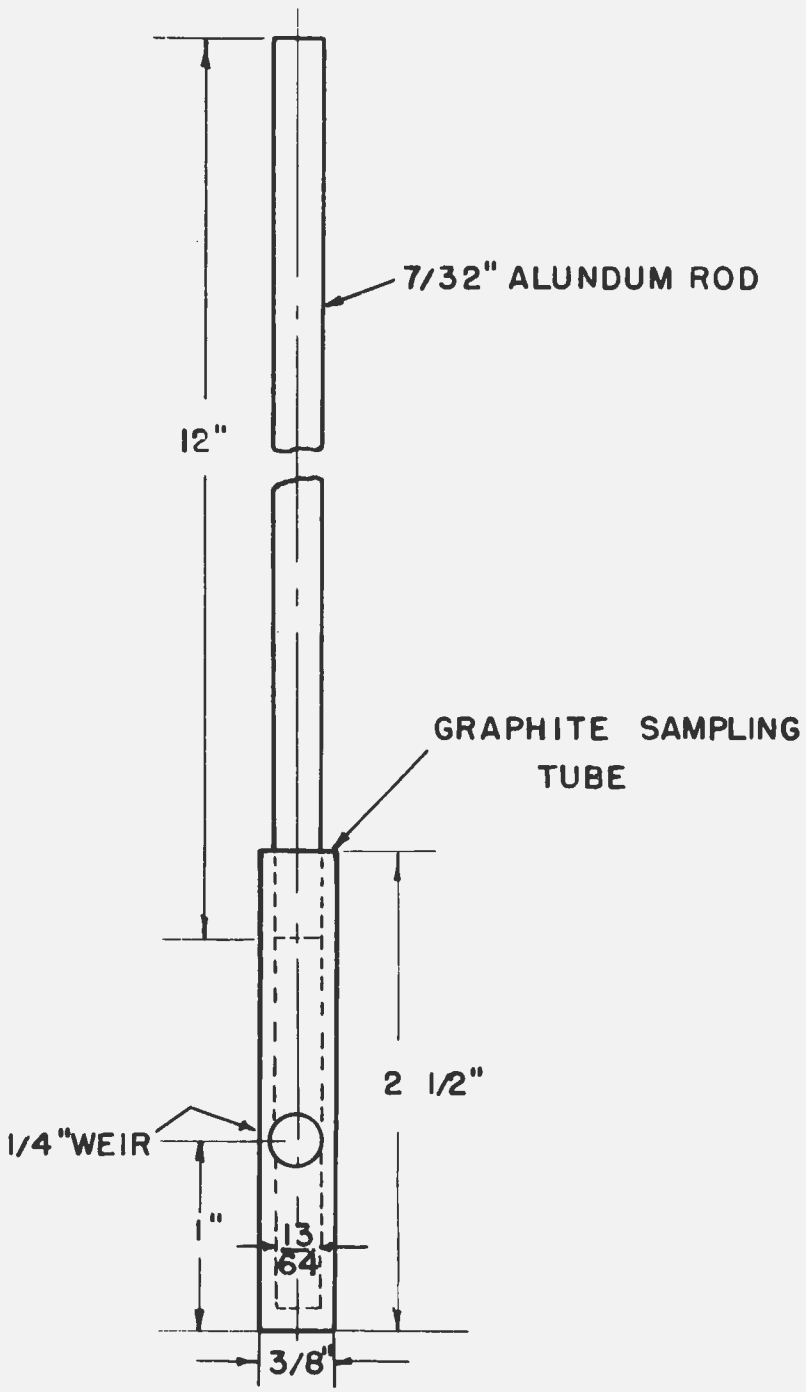

FIGURE 10. DETAILS OF LIQUID MELT SAMPLER

Table 9

Data on the Solubility of Uranium in Liquid Antimony

Furnace Charge			Equilibration		Analysis of Samples			
Grams U	Grams Solvent	Per Cent Uranium	Temp. °C.	Time Min.	Total Weight	Aliquot Weight	Mg. U	Per Cent Uranium
67	670	9.1	953.7	30	2.4396	0.2440	7.72	3.17
				60	1.6792	0.2399	6.77	2.82
				90	2.0076	0.2231	6.30	2.83
			846.4	30	2.1876	0.2430	3.97	1.64
				60	1.4646	0.2441	4.06	1.66
				90	1.6425	0.2346	3.91	1.67
			753.0	30	1.7944	0.2243	2.26	1.01
				60	1.8410	0.2301	1.94	0.84
				90	2.0091	0.2511	1.50	0.60

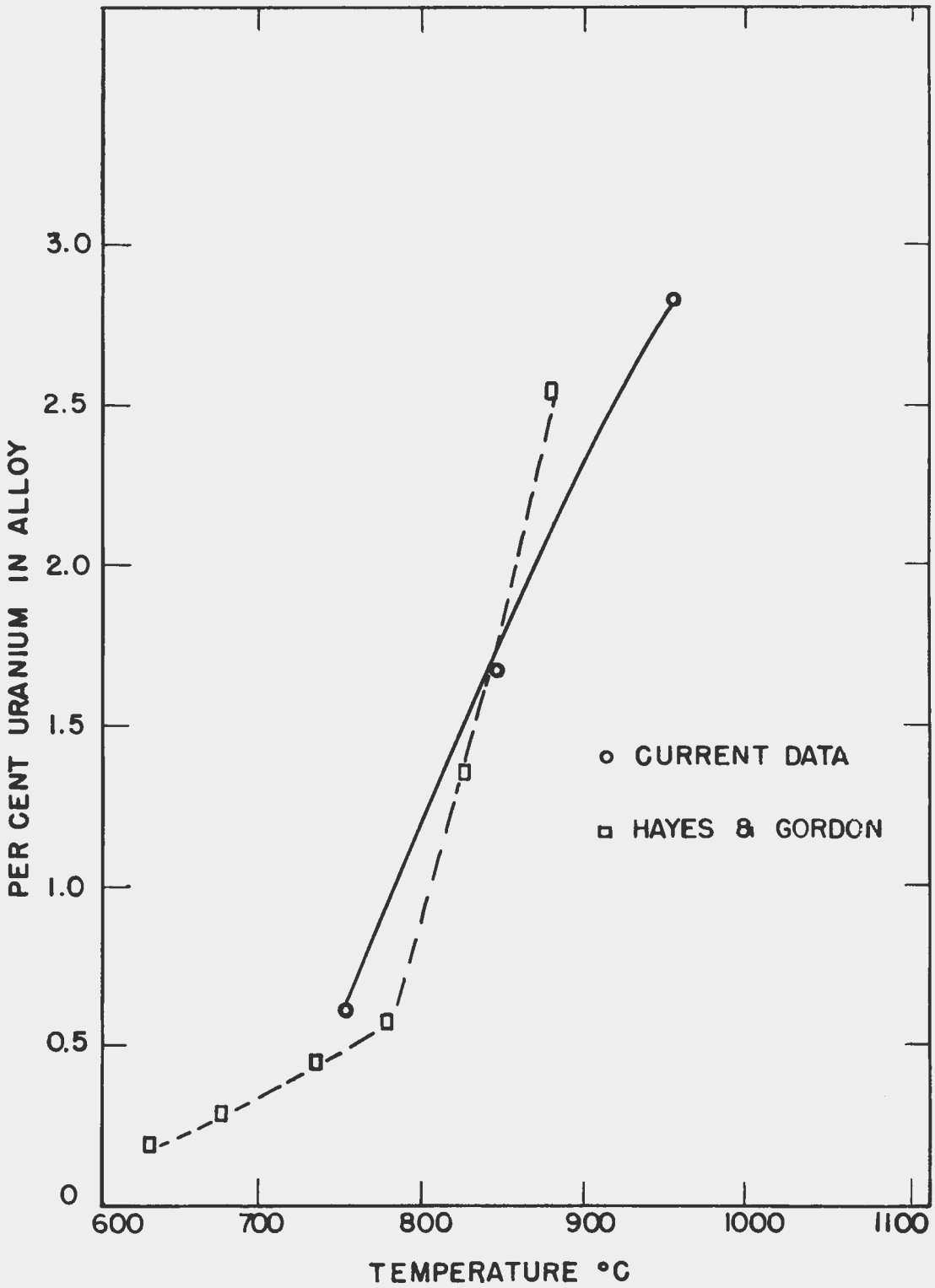

FIGURE 11. PRESENTATION OF DATA FOR THE SOLUBILITY OF URANIUM IN LIQUID ANTIMONY

the solubility curve at higher temperatures.

Solubility of uranium in bismuth

The data obtained for the solubility of uranium in bismuth are tabulated in Table 10. Figure 12 presents the data obtained, with the Hayes and Gordon, Brookhaven and National Nuclear Energy Series phase diagram data also plotted for comparison. The 120 minute value is plotted at 898.9°C. The 90 and 120 minute values at 798.2°C. are rejected, and the value at 60 minutes is plotted. At 690.7°C. the value at 120 minutes is plotted. At 609.1°C., the value at 90 minutes is plotted, and at 502.2°C. the value at 120 minutes is plotted. These data lie below the Hayes and Gordon data in the high temperature range, but agree well with interpolated values from the binary phase diagram. The solubility curve lies above the Brookhaven data at all points of comparison.

Solubility of uranium in lead

Table 11 and Figure 13 present the data obtained for the solubility of uranium in lead. The Hayes and Gordon data and Maskrey and Frost phase diagram data are also plotted for comparison. Although the settling data for the melt at the two temperatures are quite scattered, the values at 120 minutes agree with the Hayes and Gordon data. It is seen that the solubility curve falls well below the curve obtained by interpolation of the Maskrey and Frost phase diagram.

Solubility of uranium in silver

Table 12 and Figure 14 present the data obtained for the solubility of uranium in silver. The 5.0 per cent eutectic value reported by Buzzard, and the data previously reported by Ames Laboratory are plotted for comparison. The 90 minute values are seen to be close to the solid solubility of 0.1 to 0.4 weight per cent reported by Buzzard. Factors which could depress the solubility of uranium in liquid silver in this case are insufficient mixing during the solvent saturation period, oxidation of the melt, and incomplete melting of the uranium during the solvent saturation period.

Solubility of uranium in tin

The data obtained for the solubility of uranium in tin are presented in Table 13 and Figure 15. The values at 120 minutes are plotted in each case. The Hayes and Gordon and National Nuclear Energy Series phase diagram data are also plotted for comparison. The data obtained agree with the Hayes and Gordon data, in the range where comparison is possible. However, the data are well below the values interpolated from the established phase diagram.

Table 10

Data on the Solubility of Uranium in Liquid Bismuth

Furnace Charge			Equilibration		Analysis of Samples			
Grams U	Grams Solvent	Per Cent Uranium	Temp. °C.	Time Min.	Total Weight	Aliquot Weight	Mg. U	Per Cent Uranium
277	866	24.2	898.9	30	2.5713	0.2571	34.2	13.3
				60	3.8226	0.2548	34.2	13.4
				90	4.4810	0.2489	32.1	12.9
				120	4.5741	0.2541	32.8	12.9
			798.2	30	3.6148	0.2582	19.3	7.5
				60	3.7716	0.2514	17.0	6.8
				90	3.3922	0.2423	19.7	8.1
				120	3.7065	0.2471	24.8	10.0
			690.7	30	3.7958	0.2531	10.1	4.0
				60	3.2597	0.2507	6.5	2.6
				90	3.1292	0.2407	14.2	5.9
				120	3.2811	0.2524	8.1	3.2

Table 10 (Continued)

Furnace Charge			Equilibration		Analysis of Samples			
Grams U	Grams Solvent	Per Cent Uranium	Temp. °C.	Time Min.	Total Weight	Aliquot Weight	Mg. U	Per Cent Uranium
			609.1	30	3.5472	0.2534	4.3	1.7
				60	3.6046	0.2575	4.1	1.6
				90	1.7057	0.2437	4.7	1.9
				120	3.5882	0.2563	8.8	3.4
			502.2	30	1.6498	0.2357	4.8	2.0
				60	1.3710	0.2285	3.6	1.6
				90	1.3432	0.2686	4.4	1.6
				120	1.5999	0.2667	4.4	1.6

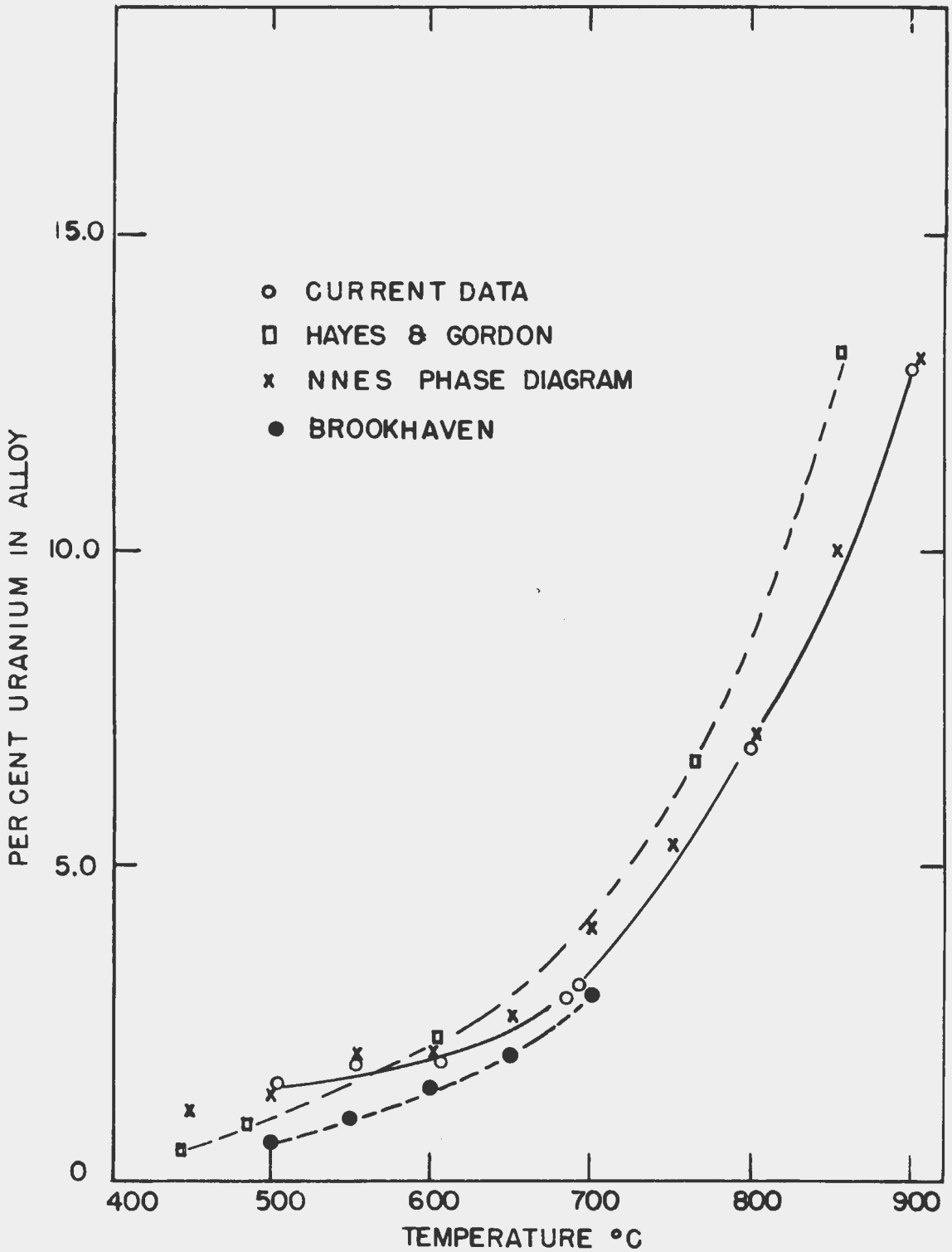

FIGURE 12. PRESENTATION OF DATA FOR THE SOLUBILITY OF URANIUM IN LIQUID BISMUTH

Table 11

Data on the Solubility of Uranium in Liquid Lead

Furnace Charge			Equilibration		Analysis of Samples			
Grams U	Grams Solvent	Per Cent Uranium	Temp. °C.	Time Min.	Total Weight	Aliquot Weight	Mg. U	Per Cent Uranium
60	1149	5.0	805.4	30	4.2779	0.2156	1.74	0.69
				60	4.2710	0.2512	1.10	0.44
				90	4.2758	0.2512	0.88	0.35
				120	4.5304	0.2517	0.50	0.20
			604.5	30	4.6654	0.2455	0.75	0.30
				60	4.3630	0.2566	0.56	0.22
				90	4,6857	0.2466	0.69	0.28
				120	4.6363	0.2576	0.28	0.11

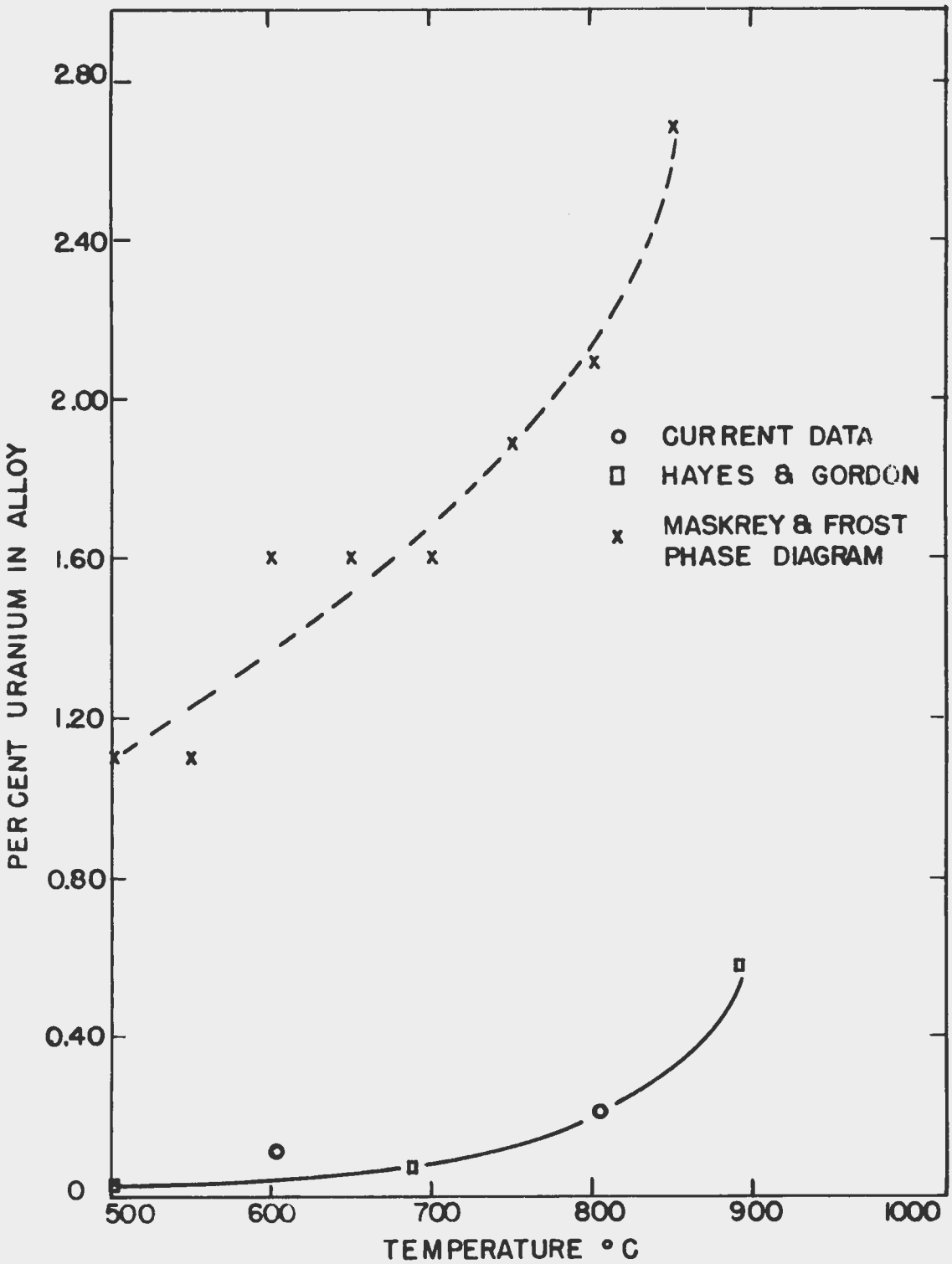

FIGURE 13. PRESENTATION OF DATA FOR SOLUBILITY OF URANIUM IN LIQUID LEAD.

Table 12

Data on the Solubility of Uranium in Liquid Silver

Furnace Charge			Equilibration		Analysis of Samples			
Grams U	Grams Solvent	Per Cent Uranium	Temp. °C.	Time Min.	Total Weight	Aliquot Weight	Mg. U	Per Cent Uranium
31	500	5.8	1109.6	30	1.9406	0.2772	0.21	0.08
				60	1.4960	0.2493	0.29	0.12
				90	2.2628	0.2514	0.21	0.08
			1051.6	30	1.6668	0.2381	0.21	0.09
				60	2.0852	0.2607	0.18	0.07
				90	1.5441	0.2574	0.21	0.08
			991.0	30	2.5626	0.2563	0.20	0.08
				60	1.9412	0.2427	0.17	0.07
				90	2.5978	0.2598	0.27	0.10

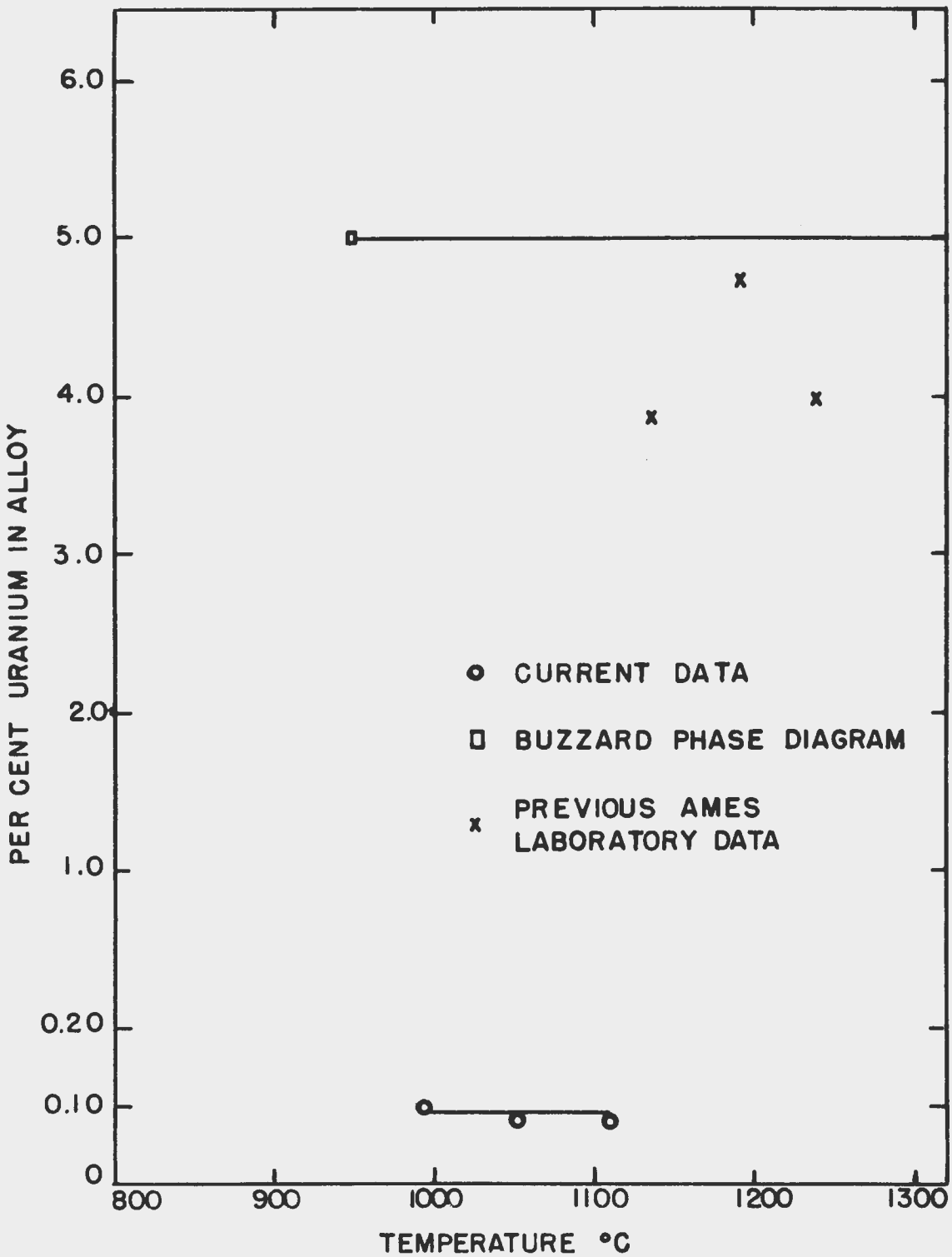

FIGURE 14. PRESENTATION OF DATA FOR THE SOLUBILITY OF URANIUM IN LIQUID SILVER

Table 13

Data on the Solubility of Uranium in Liquid Tin

Furnace Charge			Equilibration		Analysis of Samples			
Grams U	Grams Solvent	Per Cent Uranium	Temp. °C.	Time Min.	Total Weight	Aliquot Weight	Mg. U	Per Cent Uranium
69	581	10.0	1006.6	30	3.0640	0.2553	16.0	6.3
				60	3.5888	0.2563	17.4	6.8
				90	1.0342	0.2586	17.2	6.6
				120	2.9677	0.2473	15.6	6.3
			904.8	30	2.6764	0.2676	8.7	3.3
				60	2.9033	0.2419	7.6	3.1
				90	2.7060	0.2460	5.0	2.0
				120	2.7498	0.2500	3.6	1.4
			784.1	30	2.6446	0.2654	0.9	0.3
				60	2.8653	0.2605	0.4	0.2
				90	2.7958	0.2542	0.3	0.1
				120	3.0415	0.2535	0.4	0.2

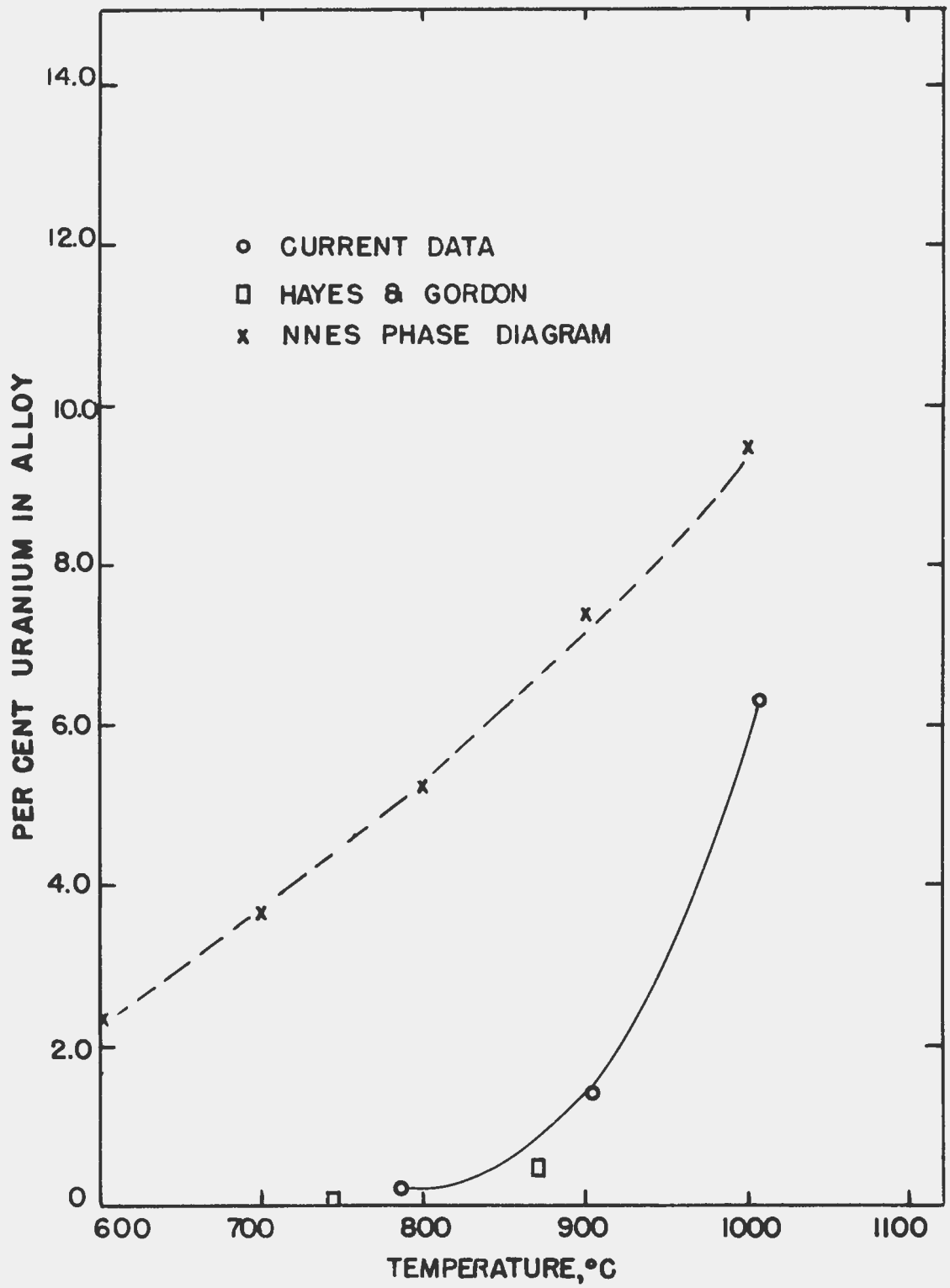

FIGURE 15. PRESENTATION OF DATA FOR THE SOLUBILITY OF URANIUM IN LIQUID TIN

High Temperature Liquid-Liquid Extraction of Uranium from Furnace Slags

It was developed previously that certain metals appeared feasible as solvents for uranium in a high temperature liquid-liquid extraction process. Figure 16 shows a proposed flow diagram for the recovery of uranium from electric furnace phosphorus slags by such a process. In step 1 the molten slag is contacted with some molten extractant. From this extractor the uranium depleted slag would be discarded, and the uranium alloy resulting from the extraction would pass to an intercooler at step 2. In the intercooler, a uranium-rich solid would be precipitated, and separated from the uranium depleted liquid. The liquid is recycled to the extractor to extract more uranium, and the solid is dissolved in nitric acid in step 3. This solution of the metals in nitric acid would serve as the feed solution to a liquid-liquid extraction step 4. The solution of the solvent metal from this step could be regenerated for return to the extractor, or sold as credit to the process. Steps 5 through 10 are conventional in a uranium production process.

As an economic basis for studying this type of process, an estimate of the chemical cost required for the process in Figure 11 was prepared. Table 14 presents the findings of this cost study for each of the metals found feasible as extractants. The assumptions made for this cost estimate were that no metal losses would occur in the extractor, and that stoichiometric quantities of chemicals would be consumed in all steps. It is seen that the proposed process has promise of economic feasibility, based on these calculations.

High temperature metal extractant studies

Initial experiments on this process were directed at contacting the molten slag with various metals. The data for these experiments are summarized in Table 15.

On the basis of radioassay analysis, bismuth and manganese appear to extract the most uranium from furnace slags by a single contact with the slag. On the basis of colorimetric analysis, lead and manganese appear to extract the most uranium. The losses of silver, manganese, lead and bismuth, upon contacting the molten slag with these metals, are high. Although no direct comparison for a given metal can be made, the increasing degree of melt agitation does not have a marked effect on the amount of extraction of uranium from the furnace slag. The per cent uranium extracted from the slags is below 50 per cent in most cases.

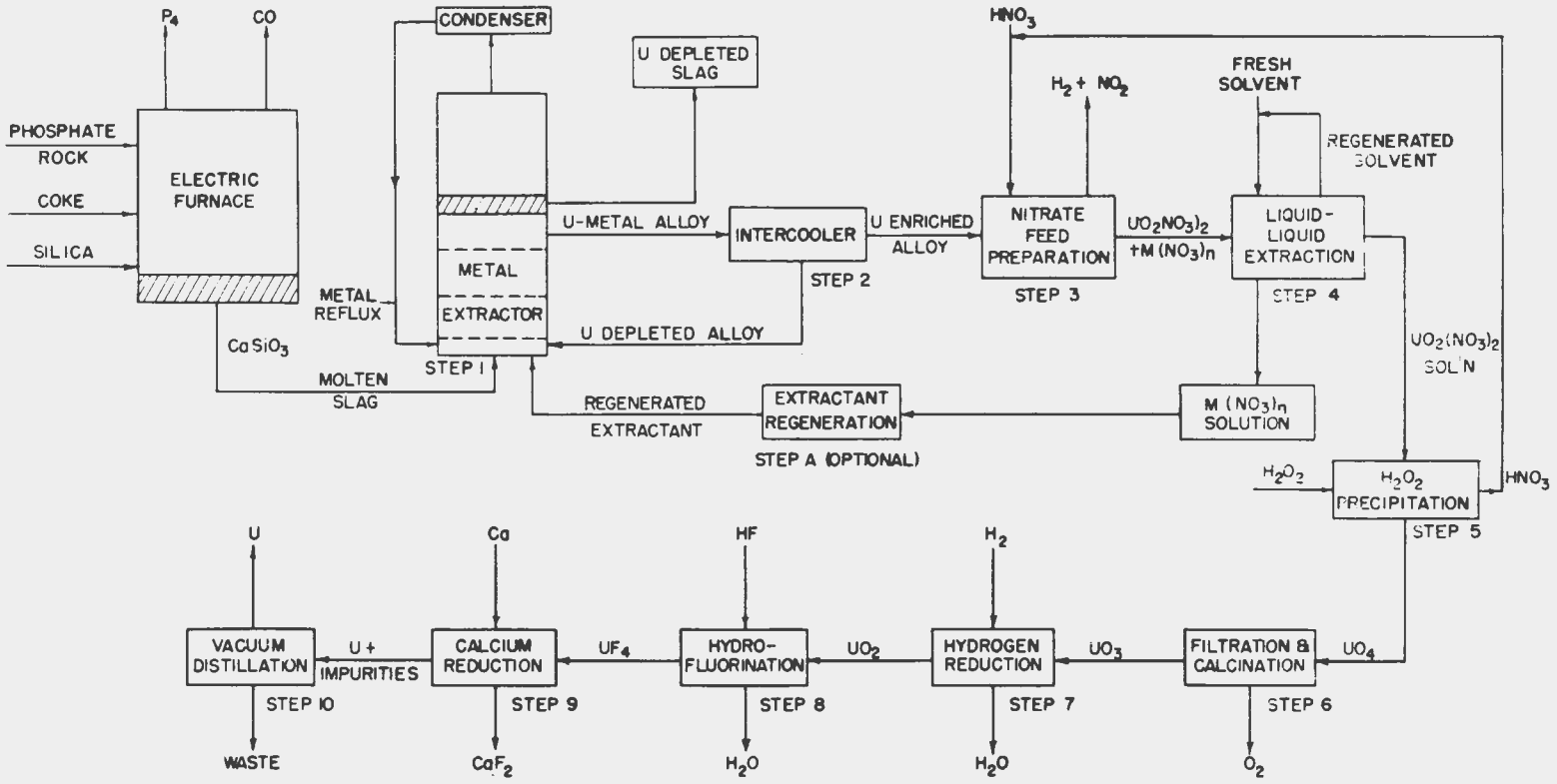

FIGURE 16. FLOW SHEET FOR PROPOSED URANIUM EXTRACTION PROCESS USING LIQUID METALS AS EXTRACTANTS

Table 14

Summary of Estimated Chemical Costs for Proposed Uranium Recovery Process Per Pound of Uranium Recovered

Step	Description of Step	Chemical Involved	Cu	Si	Sn	Pb	Bi	Mn	Fe	Co	Ni
1	Molten Metal Extraction	None - No Losses	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
2[a]	Intercooler Separation	Extractant	0.41	0.07	1.20	0.36	3.96	0.14	0.03	1.20	0.73
3	Nitrate Feed Preparation	Nitric Acid	0.60	0.36	0.33	0.42	0.42	0.51	0.30	0.34	0.38
4	Solvent Extraction	Organic Solvent Losses	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
5	Peroxide Precipitation	Hydrogen Peroxide	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
6	UO_4 Calcination	None	-	-	-	-	-	-	-	-	-
7	UO_2 Preparation	Hydrogen	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
8	UF_4 Preparation	Hydrogen Fluoride	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
9	Uranium Production	Calcium	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44
10	Vacuum Distillation	None	-	-	-	-	-	-	-	-	-
	Total without Extractant Regeneration		$1.80	$1.22	$2.32	$1.57	$5.17	$1.44	$1.12	$2.33	$1.90
	Less: Credits to Process										
4	Regenerated Extractant (100% Recovery)		$0.41	$0.07	$1.20	$0.36	$3.96	$0.14	$0.03	$1.20	$0.73
5	Nitric Acid Recovery		0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
	Plus: Estimated Chemical Costs for Extractant Regeneration		0.08	0.16	0.09	0.05	0.03	0.06	0.05	0.05	0.05
	Net Estimated Chemical Costs		$1.43	$1.27	$1.17	$1.22	$1.20	$1.32	$1.10	$1.14	$1.18

[a]Based on the separation of the following intermetallic compounds: UCu_5, USi_3, USn_3, UPb_3, UBi_2, UMn_2, UFe_2, UCo_2 and UNi_5.

Table 15

Data for High Temperature Extractant Studies

Furnace		Charge			Melt			Analysis of Slag				
	Extractant	Wt. of Solvent Grams.	Wt. of Slag - Grams	Premixing Time - min.	Temperature °F.	Hold Time - min.	Mixing	Solvent Recovered - G.	Radioassay Count	Per Cent Uranium	Colorimetric Analysis Per Cent	Per Cent Uranium Recovery Radioassay	Colorimetric
Small Globar	Iron	15.0	15.0	30	2500	15	None	-	41.3	0.0072	0.0110	26.5	-
Small Globar	Iron	26.0	14.1	None	2500	15	None	27.4	35.9	0.0063	0.0095	35.6	6.0
Small Globar	Silver	17.1	16.6	30	2500	15	None	17.0	50.0	0.0087	0.0114	11.2	-
Small Globar	Manganese	20.0	20.0	20	2500	15	None	-	44.6	0.0078	0.0036	20.4	64.4
Large Globar	Copper	143.0	50.0	None	2569	20	Crucible Rocked	145.2	47.7	0.0077	0.0084	21.4	16.9
Large Globar	Iron	130.0	75.0	None	2631	25	Crucible Rocked	131.8	48.5	0.0079	0.0099	19.4	2.0
Large Globar	Silver	50.0	25.0	None	2572	20	Crucible Rocked	49.7	42.3	0.0069	0.0072	29.6	28.7
Large Globar	Nickel	150.0	75.0	None	2569	20	Crucible Rocked	154.5	48.1	0.0078	0.0072	20.4	28.7
Large Globar	Manganese	50.0	25.0	None	2593	20	Crucible Rocked	44.8	32.8	0.0053	0.0036	45.9	64.4
Large Globar	Tin	120.0	75.0	None	2586	20	Crucible Rocked	120.1	43.1	0.0070	0.0079	28.6	21.9
Large Globar	Lead	190.0	75.0	None	2564	20	Crucible Rocked	183.9	40.6	0.0066	0.0029	32.6	71.3
Induction	Bismuth	100.0	100.0	None	2372	30	Natural Induction	95.0	33.2	0.0054	0.0102	44.9	-
Induction	Bismuth	50.0	100.0	None	2412	30	Natural Induction	46.0	47.6	0.0077	0.0163	21.4	-
Induction	Bismuth	25.0	100.0	None	2512	30	Natural Induction	22.5	46.0	0.0075	0.0095	23.5	6.0

High temperature alloy extractant studies

Although iron did not appear to extract a large portion of the uranium from the slags in the solvent studies, its relatively low cost warranted further consideration of it as an extractant. Consideration of the electromotive force series of elements shows that all of the metals considered as possible extractants for uranium, except silicon, are less electropositive than uranium, and thus would not be expected to reduce its compounds readily. It was postulated that certain reductant additions to the iron would improve the extraction of uranium from furnace slags, by selectively reducing the uranium out of the slag, and therefore improving the solubility of the uranium in the extractant. Certain experiments were performed to test the effect of adding certain elements to the melt as reductants for the uranium. In addition, manganese metal was added to tin, copper, bismuth, and lead, to test the effect of these alloys on uranium extraction. All experiments run in the induction furnace employed the crucible with impeller arrangement as shown in Figure 17. The data for these experiments are summarized in Table 16.

Mason has postulated that the enrichment of uranium in certain black shales is correlated not only with organic material, but also with the sulfur content of the shales (14, p. 153). Most of the sulfur occurs as FeS_2. With this as a theoretical basis, samples of raw Westvaco slag were contacted with molten iron sulfides, and certain other alloys of iron with non-metallic elements. All of these experiments were run in the large Globar furnace. The data obtained are presented in Table 17.

The addition of calcium, magnesium, aluminum and potassium to the iron extractant appears to improve the uranium extraction on the basis of colorimetric analysis data. The addition of elements lying between uranium and silicon in the electromotive force series appears to have a significant effect on uranium extraction based on radioassay data, but no effect based on colorimetric data. In these studies also, increasing the agitation of the melt does not have a marked effect on the amount of uranium extraction. The per cent uranium extraction is 50 per cent or below in most cases.

Among the alloys of iron with non-metallic elements, the iron sulfides extract the most uranium based on both radioassay and colorimetric data. This fact is of significance because of the natural sources of cheap sulfides such pyrites. The count of the extractant phase also indicates that uranium is being extracted by these materials. However, this phenomenon may also be a mixing effect rather than actual transfer of uranium between the two phases.

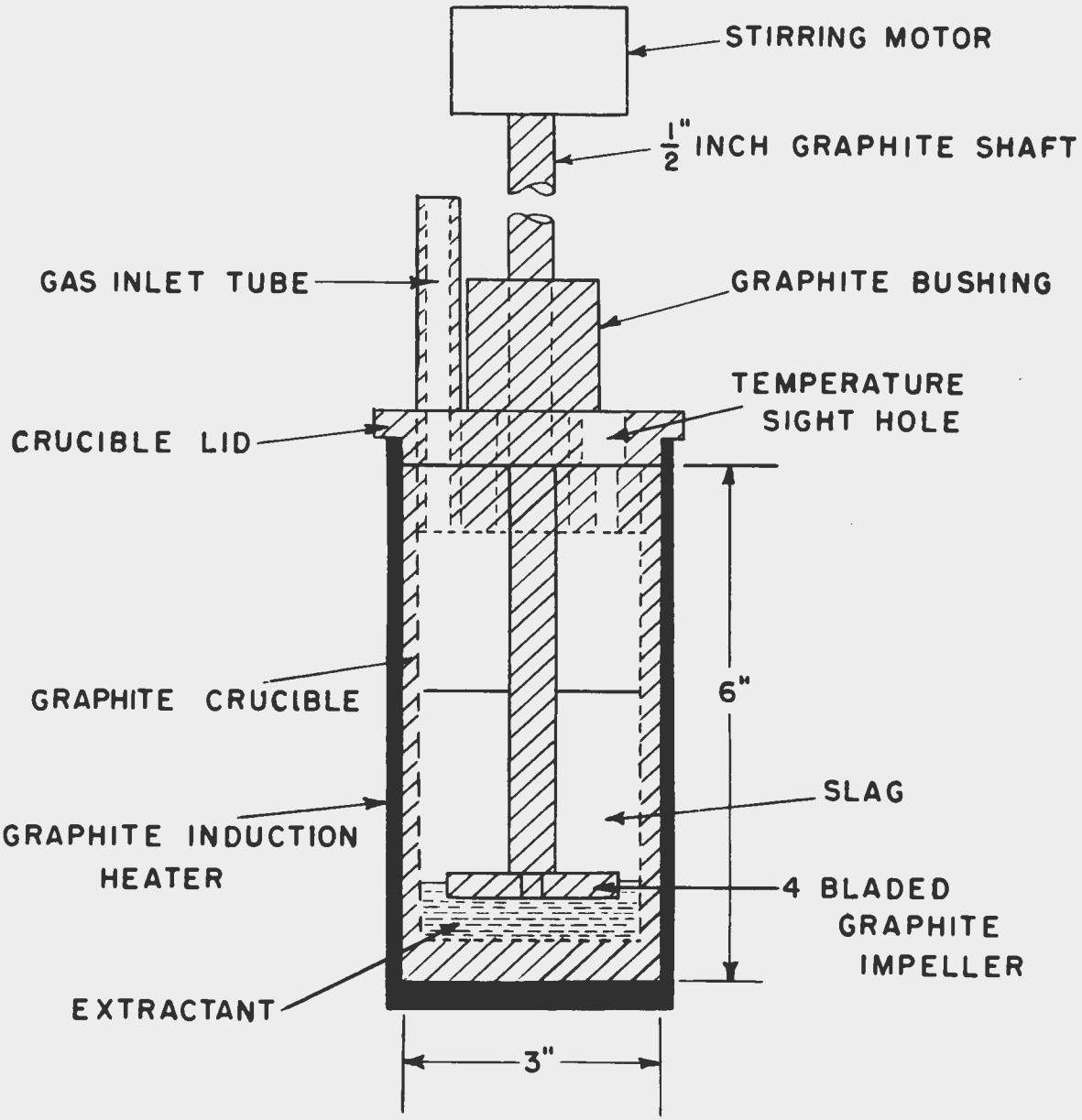

FIGURE 17. DETAILS OF INDUCTION FURNACE CRUCIBLE WITH IMPELLER MIXING

Table 16

Data for Iron Extractions of Electric Furnace Slag with Reducing Agents Added

Furnace	Charge						Melt				Analysis of Slag			Per Cent Uranium Recovery	
	Extractant	Wt. Extractant - G.	Reductant	Wt. Reductant - G.	Wt. of Slag -G.	Premixing - min.	Temperature °F	Hold time -min	Mixing	Extractant Recovered- G.	Radioassay Count	Per cent Uranium	Colorimetric Analysis	Radioassay	Colorimetric
Large Globar	Iron	50.0	Calcium	1.0	50.0	15	2450	60	None	-	42.9	0.0075	0.0058	23.5	42.5
Large Globar	Iron	1.2	Calcium	0.6	50.0	15	2461	60	None	1.0	43.4	0.0070	0.0040	28.5	60.4
Large Globar	Iron	1.2	Magnesium	0.6	50.0	15	2603	60	None	0.5	45.8	0.0075	0.0050	23.5	10.3
Large Globar	Iron	1.2	Aluminum	0.6	50.0	15	2611	60	None	1.4	51.9	0.0084	0.0058	14.3	42.5
Large Globar	Iron	1.2	Potassium	0.6	50.0	15	2537	60	None	0.6	49.5	0.0080	0.0062	18.4	38.6
Large Globar	Iron	1.2	Magnesium	0.05	50.0	15	2553	20	Crucible Rocked	1.1	53.5	0.0084	0.0068	14.3	32.6
Large Globar	Iron	0.6	Magnesium	0.02	50.0	15	2625	30	Crucible Rocked	0.7	54.5	0.0086	0.0083	12.1	17.9
Large Globar	Iron	1.2	Magnesium	0.12	100.0	15	2555	30	Crucible Rocked	-	53.6	0.0085	0.0095	13.3	6.0
Large Globar	Iron	75.0	Calcium Carbon	0.5 1.5	25.0	15	2637	40	Crucible Rocked	75.3	39.9	0.0063	0.0053	35.6	47.5
Large Globar	Iron	1.2	Magnesium Silicon	0.12 0.06	100.0	15	2536	40	Crucible Rocked	-	55.1	0.0087	0.0079	11.1	21.9
Large Globar	Iron	1.2	Magnesium Manganese	0.12 0.06	100.0	15	2546	40	Crucible Rocked	-	48.5	0.0077		21.4	
Induction	Iron	200.0	-	-	400.0	None	2792	10	Impeller	204.4	36.9	0.0060	0.0057	38.7	4.0
Induction	Iron	200.0	Manganese	2.0	400.0	None	2732	10	Impeller	196.1	38.1	0.0062	0.0041	36.7	59.4
Induction	Iron	200.0	Chromium	2.0	400.0	None	2732	10	Impeller	204.0	37.5	0.0061	0.0148	37.7	-
Induction	Iron	200.0	Vanadium	2.0	400.0	None	2772	10	Impeller	212.9	45.0	0.0073	0.0098	25.5	3.0
Induction	Iron	200.0	Molybdenum	2.0	400.0	None	2322	10	Impeller	199.8	52.2	0.0085	0.0111	13.3	-
Induction	Iron	200.0	Titanium	2.0	400.0	None	2322	10	Impeller	206.7	40.5	0.0066	0.0121	32.6	-
Induction	Iron	200.0	Manganese	2.0	400.0	None	2322	10	Impeller	215.2	46.4	0.0075	0.0104	23.5	-
Induction	Tin	200.0	Manganese	2.0	400.0	None	2542	10	Impeller	201.6	41.0	0.0067	0.0048	31.6	52.5
Induction	Copper	200.0	Manganese	2.0	400.0	None	2542	10	Impeller	208.5	38.8	0.0063	0.0092	35.6	9.0
Induction	Bismuth	200.0	Manganese	2.0	400.0	None	2372	10	Impeller	188.5	41.1	0.0067	0.0028	31.6	72.2
Induction	Lead	200.0	Manganese	2.0	400.0	None	2542	10	Impeller	195.0	39.4	0.0064	0.0075	34.6	25.9

Table 17

Data for Extractions of Furnace Slags with Alloys of Iron with Non-Metallic Elements

Charge					Melt			Analysis of Slag			Per Cent Uranium Recovery		Radio-assay of Extractant c/m over BG
Extractant	G.	Reductant	G. Reductant	G. Slag	Temp. °F.	Hold Time -min.	Mixing	Radio-assay Count	Per Cent Uranium	Colorimetric Analysis	Radio-assay	Colorimetric	
Fe_2O_3	25.0	Mg	0.05	25.0	2554	20	Crucible Rocked	44.4	0.0070	0.0080	28.6	20.8	-
FeP	25.0	Mg	0.05	25.0	2565	30	Crucible Rocked	55.6	0.0088		10.1		0.2
FeS	25.0	Mg	1.0	25.0	2520	20	Crucible Rocked	31.7	0.0050		49.0		9.0
FeS_2	25.0	Mg	0.05	25.0	2404	30	Crucible Rocked	35.9	0.0057	0.0055	41.9	45.5	11.0

Multiple contact extractions of furnace slag

Because calcium appeared the best reducing agent in conjunction with iron as an extractant, an experiment was run to study the effect of multi-stage contact of one portion of slag with several portions of new extractant. The data obtained from this experiment are presented in Table 18. The large Globar furnace was used for all of these contacts.

Although bismuth is an expensive metal, it appeared to have the highest capacity for uranium of any of the metals that could be used as uranium extractants. To further study bismuth as an extractant, the experiment described in Figure 18 was performed. A sample of bismuth was successively contacted with several portions of raw slag, and the first portion of slag successively contacted with two more portions of fresh bismuth. In this manner an estimate of the limit of extraction by the bismuth, and from the slag, could be made. For the contacts, the induction furnace and crucible arrangement of Figure 17 were used. The data obtained are presented in Table 19.

Iron sulfides warranted further study as extractants for uranium, because of the high recoveries obtained in the above study. The multiple contact experiment shown in Figure 19 was performed. All contacts were made in the large Globar furnace. The data obtained are summarized in Table 20.

Contacting the molten slag with successive batches of iron-calcium extractant does not successively increase the amount of uranium extraction from a portion of furnace slag. The amount of extraction is well below 50 per cent. For the multiple contacts of one portion of bismuth with successive portions of raw furnace slag, the bismuth successively extracts some of the uranium from the slag. The amount of extraction is below 50 per cent. Additional contacts of the slag from stage 1 with two more portions of raw bismuth does not improve the uranium extraction from this portion of the slag.

The bismuth losses in these contacts are quite high. Although the radioassay count of the bismuth indicates extraction of uranium in each case, the trend of these counts can not be matched with the corresponding trend in the uranium analysis of the furnace slag.

For the multiple contacts of furnace slag with iron sulfides, it is seen that one portion of sulfide extracts successively smaller amounts of uranium from three successive portions of raw furnace slag, as shown along stages 1, 2 and 3. This indicates a limit to the amount of uranium that one portion of sulfide could extract. The same trend occurs along stages 4, 5 and 6. The successive extractions along this path are less than along stages 1, 2 and 3. Along stages 1, 4 and 7, the successive fresh portions of sulfide extract less uranium in successive contacts. This indicates a limit to the amount of uranium that could be extracted from one portion of furnace slag.

Table 18

Data for Multiple Contacts of Electric Furnace Slag with Iron-Calcium Extractant

Stage	Charge			Melt				Analysis of Slag			Per Cent Uranium Recovery	
	Grams Iron	Grams Calcium	Premix Time min	Grams Slag	Temp. °F	Hold Time	Mixing	Iron Recovered Grams	Radioassay Count	Per Cent Uranium	Colorimetric Analysis	Radioassay	Colorimetric
1	6.0	0.3	15	50.0	2593	60 min	Crucible Rocked	6.1	44.4	0.0072		26.5	
2	6.0	0.6	None	47.7 Stage 1	2582	60 min	Crucible Rocked	6.6	38.5	0.0063		35.7	
3	6.0	None	None	46.7 Stage 2	2635	60 min	Crucible Rocked	6.3	45.5	0.0074	0.0098	24.5	3.0
1A	12.0	0.6	15	50.0	2575	60 min	None	11.9	43.3	0.0070		28.5	
2A	12.0	0.6	None	47.9 Stage 1A	2575	60 min	None	12.3	47.5	0.0077		21.4	
3A	12.0	None	None	46.0 Stage 2A	2606	60 min	None	12.1	46.5	0.0075	0.0038	23.5	62.4

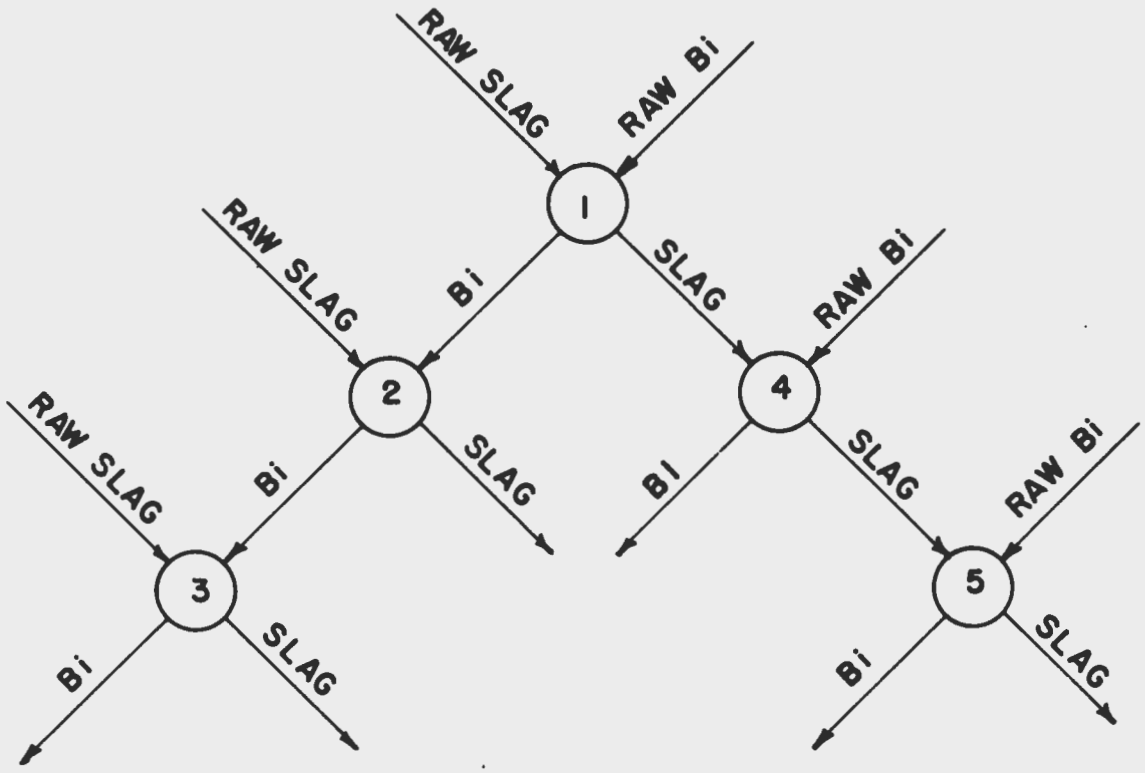

FIGURE 18. DIAGRAM OF CONTACTS FOR MOLTEN BISMUTH EXTRACTION OF RAW WESTVACO SLAG

Table 19

Data for Multiple Contacts of Electric Furnace Slag with Bismuth

Diagram No. Fig. 20	Charge G. Bi	Charge G. Slag	Melt Temp. °F.	Melt Hold Time -min.	Melt Mixing	Bi Recovered G.	Per Cent Bi Loss	Analysis of Slag Radioassay Count	Analysis of Slag Per Cent Uranium	Analysis of Slag Colorimetric analysis	Per Cent Uranium Recovery Radioassay	Per Cent Uranium Recovery Colorimetric	Radioassay Count of Bi c/m over BG
1	200.0 raw	400.0 raw	2372	10	Impeller	196.0	2.0	40.2	0.0065	0.0081	33.6	19.9	7.1
2	189.5 #1	400.0 raw	2372	10	Impeller	177.0	6.6	37.7	0.0061	0.0064	37.7	36.6	8.6
3	166.0 #2	400.0 raw	2372	10	Impeller	150.0	10.0	34.0	0.0055	0.0083	43.9	17.8	7.2
4	200.0 raw	386.0 #1	2372	10	Impeller	196.0	2.0	42.2	0.0069	0.0059	27.5	41.6	11.5
5	200.0 raw	369.0 #2	2372	10	Impeller	196.5	1.7	46.4	0.0075	0.0077	23.5	23.9	24.7

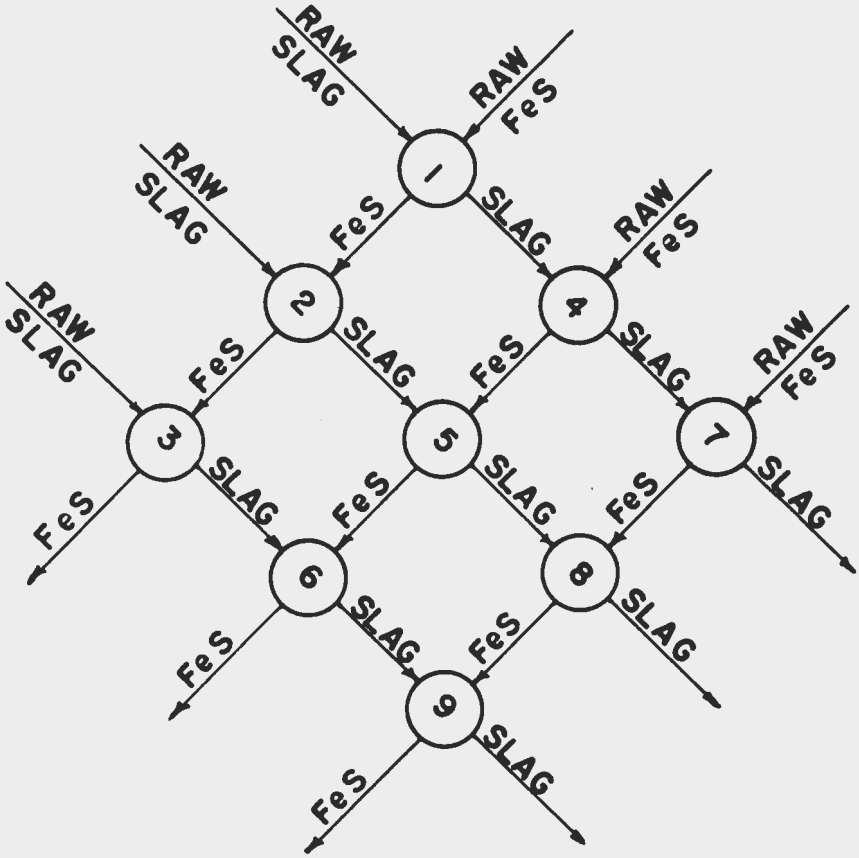

FIGURE 19. ARRANGEMENT OF STAGES FOR MULTIPLE CONTACT OF IRON SULFIDE WITH FURNACE SLAG

Table 20

Data for Multiple Contacts of Furnace Slag with Molten Iron Sulfide

Stage Number	Charge				Melt			Radioassay Count of Sulfide c/m over BG
	G. Slag	G. FeS	Temp. °F.	Contact Time - min	Mixing	G. Slag Recovered	G. FeS Recovered	
1	50.0 raw	50.0 raw	2550	20	Crucible Rocked	47.3	51.5	7.0
2	50.0 raw	50.0 Stage 1	2550	20	Crucible Rocked	49.0	51.5	12.4
3	50.0 raw	51.7 Stage 2	2550	20	Crucible Rocked	56.8	50.0	13.0
4	47.3 Stage 1	50.0 raw	2550	20	Crucible Rocked	46.1	49.9	4.9
5	49.0 Stage 2	50.1 Stage 4	2550	20	Crucible Rocked	49.3	49.3	7.8
6	46.1 Stage 3	49.3 Stage 5	2550	20	Crucible Rocked	55.9	48.9	10.2
7	46.1 Stage 4	50.0 raw	2550	20	Crucible Rocked	46.0	48.8	1.4

Distribution of uranium between bismuth and furnace slag

The success of the high temperature extraction of uranium from these slags using liquid metals in the proposed process depends on attaining a suitable concentration of uranium in any given metal. Successive batch contacts of slag with bismuth in an attempt to build up any sizeable concentration of uranium from the slag in the bismuth would take a large number of contacts. Therefore, a study of the distribution of uranium between Westvaco slag and bismuth metal was made. To do this, various amounts of uranium oxides, to simulate U_3O_8, were added to the melt. The slag, metal and oxide were heated in a graphite crucible with the induction heater. The melt was stirred for seven minutes with the graphite stirring impeller. After the contact was made, the slag phase was pulverized and analyzed for uranium. Table 21 summarizes the data obtained.

Table 22 summarizes the material balances, distribution coefficients, and desired distribution coefficients obtained in the study of uranium distribution between bismuth and furnace slag. It is seen that the actual distribution coefficients on the basis of both radioassay and colorimetric data lie far below those required for a successful process.

Solubilizing Fusion Treatments of Furnace Slag

Latimer and Hildebrand discuss the general chemistry of uranium (10, p. 364). For +4 uranium compounds, they report that the halides are water soluble, except for UF_4. For the +6 compounds, the uranyl ion forms slightly soluble compounds with phosphates, arsenates, double alkali carbonates, sulfites, complex alkali fluorides and sulfides. Uranyl halides, acetate, sulfate and nitrate are water soluble.

A process in which the molten slag would be fused with some additive to yield one of these compounds, crushed after solidification and water leached to recover the uranium was considered. To simulate such a process, samples of Westvaco slag were fused with various inorganic compounds, and the crushed fusion residue leached with water.

The slag and additive were mixed for 30 minutes, and fused in the gas fired furnace at 2200°F. for ten minutes. The residue was pulverized to 65 mesh and leached in hot water for three hours. The residue was filtered off, washed with water, and dried in an oven at 110°C. The dried residue was pulverized and radioassayed. The data obtained are summarized in Table 23.

The only solubilizing fusion treatment which resulted in any appreciable elimination of uranium from the slag was the one with calcium chloride.

Table 21

Data for Study of Uranium Distribution between Furnace Slag and Liquid Bismuth

Charge				Melt				Analysis of Slag		
G. Bi	G. Slag	G. UO_2	G. UO_3	Temp. °F.	Impeller Mixing Time -min.	G. Bi Recovered	G. Slag Recovered	Radio-assay Count	Per Cent Uranium	Colorimetric Analysis
200.0	400.0	0.0389	0.0789	2372	7	180.4	394.2	101.8	0.0165	0.0257
200.0	400.0	0.1958	0.4251	2372	7	185.8	396.2	375.6	0.0609	0.0780
200.0	400.0	0.3830	0.8005	2372	7	194.6	397.4	723.9	0.1175	0.1165
200.0	400.0	0.7580	1.6031	2372	7	187.8	395.0	1304.9	0.2120	0.2849
200.0	400.0	1.1369	2.4049	2372	7	174.1	393.8	1901.0	0.3086	0.4899

Table 22

Material Balances, Distribution Coefficients and Desired Distribution Coefficients for Study of Uranium Distribution Between Electric Furnace Slag and Bismuth

A. Radioassay Data

Uranium Input - Micrograms					Uranium Output - Micrograms			Micrograms U / Gram Bi	Micrograms U / Gram Slag	$\kappa = \frac{\gamma U / G. Bi}{\gamma U / G. Slag}$
Slag	Bi	UO_2	UO_3	Total	Slag	Bi	Total			
39,200	0.0	34,260	65,650	139,110	63,850	75,260	139,110	417	162	2.58
39,200	0.0	172,400	353,600	565,200	238,600	326,600	565,200	1,760	602	2.92
39,200	0.0	337,800	666,000	1,043,000	461,000	582,000	1,043,000	2,996	1,160	2.58
39,200	0.0	668,500	1,334,000	2,041,700	826,500	1,215,200	2,041,700	6,470	2,094	3.09
39,200	0.0	1,002,000	2,004,000	3,045,200	1,200,000	1,845,200	3,045,200	10,600	3,046	3.48

B. Colorimetric Data

Uranium Input - Micrograms					Uranium Output - Micrograms			Micrograms U / Gram Bi	Micrograms U / Gram Slag	$\kappa = \frac{\gamma U / G. Bi}{\gamma U / G. Slag}$
Slag	Bi	UO_2	UO_3	Total	Slag	Bi	Total			
40,400	0.0	34,260	65,650	140,310	101,200	39,110	140,310	217	257	0.84
40,400	0.0	172,400	353,600	566,400	308,600	257,800	566,400	1,389	779	1.78
40,400	0.0	337,800	666,000	1,044,200	463,500	580,700	1,044,200	2,984	1,167	2.56
40,400	0.0	668,500	1,334,000	2,042,000	1,124,000	918,000	2,042,000	4,890	2,846	1.72
40,400	0.0	1,002,000	2,004,000	3,046,400	1,928,000	1,118,400	3,046,400	6,410	4,900	1.31

C. Calculation of κ Values Required for Feasible Process

Per cent Uranium in Final Alloy	25 Per Cent Uranium Recovery			50 Per Cent Uranium Recovery			75 Per Cent Uranium Recovery		
	γU/G. Slag	γU/G. Bi	κ	γU/G. Slag	γU/G. Bi	κ	γU/G. Slag	γU/G. Bi	κ
1.0	75.0	10,110	135	50.0	10,110	202	25.0	10,110	405
2.0	75.0	20,420	272	50.0	20,420	409	25.0	20,420	816
3.0	75.0	30,940	412	50.0	30,440	619	25.0	30,940	1,240
5.0	75.0	52,600	701	50.0	52,600	1,051	25.0	52,600	2,100

Table 23

Data for Solubilizing Fusion Treatments of Furnace Slag

Additive	Slag Additive Ratio	Radioassay of Leached Residue	Per Cent Uranium	Colorimetric Analysis Per Cent	Per Cent Uranium Recovery	
					Radio-assay	Colori-metric
Na_2CO_3	4.0	44.2	0.0077		21.4	
NaCl	4.0	52.4	0.0091		7.1	
$Al_2(SO_4)_3$	4.0	51.5	0.0090	0.0184	8.1	-
$BaCl_2 \cdot 2H_2O$	4.0	44.5	0.0078	0.0087	20.4	13.9
$Ba(OH)_2 \cdot 8H_2O$	4.0	51.0	0.0089	0.0112	9.1	-
H_3BO_3	4.0	48.6	0.0085	0.0093	13.1	8.0
$AlK(SO_4)_2 \cdot 12H_2O$	4.0	65.2	0.0114		-	
$CaCl_2$	4.0	32.6	0.0057		41.9	

It is not known whether the uranium was solubilized by the treatment, or eliminated from the slag by volatilization.

Miscellaneous Treatments of Furnace Slag

It was observed that a small fraction of the raw furnace slags was magnetic. Since the uranium could be present as some intermetallic compound or alloy of iron or nickel, a separation of this phase was performed, and the sample obtained analyzed for uranium. Four pounds of ground Westvaco slag were treated by passing the slag over a cardboard chute, arranged over the poles of a strong permanent magnet. By several passes over the magnet 3.5 grams of magnetic material were recovered, which gave a radioassay counting rate of 24.1 counts per minute over the background count.

Samples of raw Westvaco slag were leached with both inorganic and organic solvents. The finely ground slag and solution were agitated at room temperature. The residue was filtered, washed, and dried at 110°C. The dried residue was pulverized and radioassayed. The data for these experiments are presented in Table 24.

The recovered magnetic portion of furnace slag analyzed 0.1 per cent by spectrographic analysis. The 3 1/2 grams of material recovered represent 0.193 per cent of the total weight of material treated. If 100 per cent of the uranium in the slag was concentrated in the magnetic material, it would analyze 5.1 per cent uranium. It is evident that the uranium in furnace slags is not concentrated in the magnetic material.

None of the leaching agents tried extracted an appreciable amount of uranium from the slag. This is an indication that the calcium silicate lattice must be opened before the uranium can be extracted from the slag.

Cost Calculations for Exploratory Slag Treatments

Cost calculations for the exploratory treatments can only be carried through the raw materials cost, based on the data obtained in the study. Cost calculations for cases where these chemical costs lie below 100 dollars are summarized in Table 25. Based on these calculations it is evident that none of the exploratory treatments studied would result in an economic recovery process.

Table 24

Data for Miscellaneous Leaching Treatments of Furnace Slag

Leaching Agent	Diluent	Concentration of Leach Solution Per Cent	Weight of Slag Grams	Weight of Leach Solution Grams	Leach Time hr.	Analysis of Dry Residue: Radioassay Count	Analysis of Dry Residue: Per Cent Uranium	Analysis of Dry Residue: Colorimetric Analysis	Per Cent Uranium Recovery: Radioassay	Per Cent Uranium Recovery: Colorimetric
NaOH	Water	15	50.0	200.0	2	55.9	0.0097	0.0151	1.0	-
Na_2O_2	Water	10	20.0	200.0	2	60.5	0.0105	0.0120	-	-
$AlC_2H_3O_2$	Water	2	50.0	250.0	8	60.0	0.0105	0.0113	-	-
$CuNH_4Cl$	Water	-	20.0	200.0	4	60.4	0.0105	0.0081	-	19.9
OPPA[a]	Kerosene	10	50.0	150.0	1/2	63.0	0.0110	0.0105	-	-
Ether + 1% HNO_3	-	-	25.0	50.0	1	54.3	0.0095		3.1	

[a]Octyl-pyro-phosphoric acid, which has the empirical formula, $C_8H_{18}O$.

Table 25

Cost Calculations for Exploratory Slag Treatments. Basis: One Pound of Uranium Recovered

Materials		Per Cent Uranium Extraction		Weight of Slag Per Pound of Uranium Recovered	Ratio of Chemicals to Slag		Pounds Chemical Used		Cost of Chemicals Per Pound		Total Chemical Costs		
Extractant	Reductant	Radioassay	Colorimetric		Extractant	Reductant	Extractant	Reductant	Extractant	Reductant	Extractant	Reductant	Total
Iron	Magnesium	21.4		46,800	0.012	0.0012	561	56	0.03	0.21	16.83	11.76	$37.55
	Manganese					0.0006		28		0.32		8.96	
Iron	Calcium		47.5	21,000	0.012	0.0012	252	25	0.03	1.30	7.56	32.50	40.06
Iron	Calcium	35.6		28,100	0.012	0.0012	338	34	0.03	1.30	10.14	44.20	54.34
Iron	Magnesium		17.9	55,900	0.012	0.004	671	224	0.03	0.21	20.13	47.04	67.17
Iron	Magnesium	12.1		82,600	0.012	0.004	991	330	0.03	0.21	29.73	69.30	99.03
Iron	Magnesium		32.6	30,600	0.024	0.010	734	306	0.03	0.21	22.02	64.26	86.28
Iron	Aluminum		42.5	23,600	0.024	0.012	566	284	0.03	0.21	16.98	59.60	76.58

Discussion

By consideration of Figure 1, other possiblilities are seen to exist for the recovery of uranium in the overall electric furnace process for producing elemental phosphorus. As was mentioned in the introduction, some of the uranium in the furnace feed rock is volatilized during the reduction process. The compounds of uranium which are volatile include UBr_3, UBr_4, UCl_4, UF_6 and UO_2Cl_2. Since phosphate rock contains fluorine, it is possible that this portion of the uranium is volatilized as a fluoride.

Although the exact nature of uranium in the slags is not known, postulation that it occurs as UO_2, or some uranyl compound allows further speculation as to how the uranium might be volatilized during the reduction of the phosphate rock in the electric furnace. Katz and Rabinowitch (9, p. 473) list a number of reactions of UO_2 and U_3O_8 to produce volatile uranium halides. Among the chlorinating agents are a number of solid chlorides such as $CaCl_2$, $BeCl_2$, $MgCl_2$ and $AlCl_3$. These materials could be added to the furnace charge, and the volatilized uranium scrubbed into the condenser water.

The Tennessee Valley Authority reports that most of the vanadium in Western phosphate ores appears in the by-product ferrophosphorus when these ores are processed in the electric furnace (19, p. 250). Other elements that have found in ferrophosphorus include silicon, manganese, titanium, carbon, calcium, molybdenum, copper and chromium. It is thought that the percentages of these constituents in the phosphate rock feed primarily governs the amount of the elements entering the ferrophosphorus.

The composition of the ferrophosphorus is also affected by the excess carbon in the furnace charge. When highly reducing conditions exist in the furnace (high excess of coke), part of the SiO_2 is reduced to silicon, which then combines with the ferrophosphorus. Thus it may also be possible to alter furnace operating conditions such that the uranium in the phosphate rock feed will enter the ferrophosphorus. The possibility might then exist of concentrating the uranium by stripping it out of the ferrophosphorus with materials which are immiscible with ferrophosphorus, such as bismuth or lead.

Although a number of materials appear to extract uranium from furnace slag, the results of the bismuth-slag uranium distribution study make the possibility of a build-up of uranium in any extractant by successive contacts with furnace slag seem highly unlikely. This fact obviates the technical feasibility of the proposed high temperature extraction process. Suggestions for recovering the small amount of uranium extracted by a single contact with the slag include the possibility of a drossing or slagging step, or alloying the uranium with some other metal, which makes

the resultant alloy insoluble in the extractant material.

The use of manganese as an extractant or reductant warrants further consideration. Every experiment in which manganese was used resulted in relatively high uranium extraction. Postulated mechanisms are the formation of some manganite compound of uranium, which is soluble in the manganese metal or in some other extractant, or replacement of the uranium by manganese as the substituent in the calcium silicate lattice.

The high solubility of uranium in tin found in this investigation warrants re-evaluation of it as an extractant for uranium in a high temperature extraction process. Factors which would make tin a more desirable solvent than bismuth include its high boiling point (2260°C.), greater thermodynamic activity towards uranium compounds, lower cost, and lower losses by contact with molten slag.

The use of iron sulfides also warrants further consideration as an extractant, because of the low cost of these materials. A study of the distribution of uranium between the slag and sulfides, similar to the study with bismuth, is recommended for future study. The miscibility of the two materials should be studied to show whether extraction actually occurs when the two materials are contacted.

In all of the work done to date on this problem, the direct acid leaching results of Mound Laboratory give the best extractions. However, as was stated, the consumption of even sulfuric acid by the lime phase of the slag would make such a process uneconomic. Some very elementary experiments in this investigation showed that from 30 to 40 per cent of the uranium in furnace slag would be extracted by a phosphoric acid-OPPA extraction of furnace slag. This process is similar to the sulfuric acid acidulation-OPPA extraction of phosphate rock process for the recovery of uranium during the production of normal superphosphate. In such a process the phosphoric acid acidulation would serve to open up the slag, making the uranium amenable to extraction, and produce a product high in P_2O_5 content. The use of electric furnace phosphoric acid would serve as a conservation of sulfuric acid. The economics of such a process would be improved by the simultaneous extraction and recovery of some of the other more valuable constituents of the slag, such as chromium, copper, nickel and silver.

CONCLUSIONS

From data obtained in this study, the following conclusions are made:

1. The results of the thermal reduction experiments indicate that calcium and magnesium do not reduce uranium out of electric furnace phosphorus slag under the conditions studied.

2. The results of the high temperature extractant studies indicate that, of any of the extractants studied, bismuth, lead and manganese extract the most uranium from electric furnace slag by a single contact of the metal with the slag.

3. The amount of uranium extracted appears to be 50 per cent or less for most of the high temperature extraction experiments.

4. The results of the high temperature experiments where calcium, magnesium, aluminum and potassium were added to the melt as reducing agents indicate that these metals improve the uranium extraction from the furnace slag.

5. The results of the high temperature experiments where metals between uranium and silicon in the electromotive force series were added to the melt indicate that these materials improve the uranium extraction on the basis of radioassay data, but indicate that they do not improve extraction on the basis of colorimetric data.

6. The study of uranium distribution between bismuth and furnace slag indicate that the possibility of building up a sizeable concentration of uranium in bismuth by successive contacts of the metal with molten furnace slag is highly unlikely.

7. The magnetic separation experiment indicates that the uranium in electric furnace slag is not concentrated in the magnetic material of the slag.

8. The cost calculations based on exploratory data indicate that none of the recovery experiments would result in an economic recovery process.

9. The data for the solubility of uranium in lead indicate that the liquidus curve of the established lead-uranium phase diagram lies above the solubility curve determined by the mixing-settling-melt sampling technique.

10. The data for the solubility of uranium in tin indicates that the liquidus curve of the established tin-uranium phase diagram lies above the solubility curve determined by the mixing-settling-melt sampling technique.

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APPENDIX

Radioassay Analysis for Uranium in Furnace Slags

The natural radioactive property of uranium made radioassay methods of analysis for these low uranium concentration materials attractive. For this investigation, an empirical method of radioassay was developed which allowed rapid screening of exploratory results.

The equipment used for these analyses included a Radiation Laboratories Mark 3 Model 15 cylindrical shielded sample housing, and a Nuclear Instrument and Chemical Corporation Model 165 electronic scaler. All counts were made with a Tracerlab TGC-2 Geiger-Mueller tube. This tube has a mica window, with a density of less than two mg./cm.^{2}. The threshold voltage is rated at 1100 to 1250 volts, and the number of counts greater than 10^9. The quench gas used is helium.

To make an analysis, the finely crushed material (passing 80 mesh) was packed firmly into a 1 5/16 inch diameter by 1/4 inch depth cylindrical aluminum planchet. The depth of this tray was designed from data developed by Doig et al. at Battelle Memorial Institute (7). Figure 20 presents this data as counts per minute over background versus the depth of the sample, using 1 5/16 inch diameter trays, and a -325 mesh ore, analyzing 0.020 to 0.021 per cent uranium. It was concluded from this that for these materials the counting rate is independent of the sample depth for depths 1/4 inch and over.

The planchet was placed in a specially designed aluminum tray, and the tray with planchet placed in the sample housing, as close to the window of the Geiger tube as possible. Figure 21 shows the geometry of the tube and planchet in the sample housing.

When the sample had been counted for the desired length of time, the gross counting rate of the material was computed from the scaler reading, and the background count (no planchet or sample in the housing) subtracted to obtain the net counting rate. The per cent uranium in the sample was obtained by linear extrapolation from the count of a standard phosphate rock. This rock was obtained from the New Brunswick Laboratory of the Atomic Energy Commission, and analyzed 0.0246 per cent uranium (18). The count of the standard rock was taken under the same housing geometry conditions as the samples to which it was applicable. Thus, a count of the standard rock was made each time a Geiger tube was replaced, because the geometry conditions had been changed somewhat by changing the tube. Figure 22 presents the linear correlation used between counting rate and per cent uranium in the standard rock, for several replacements of the Geiger-Mueller tube.

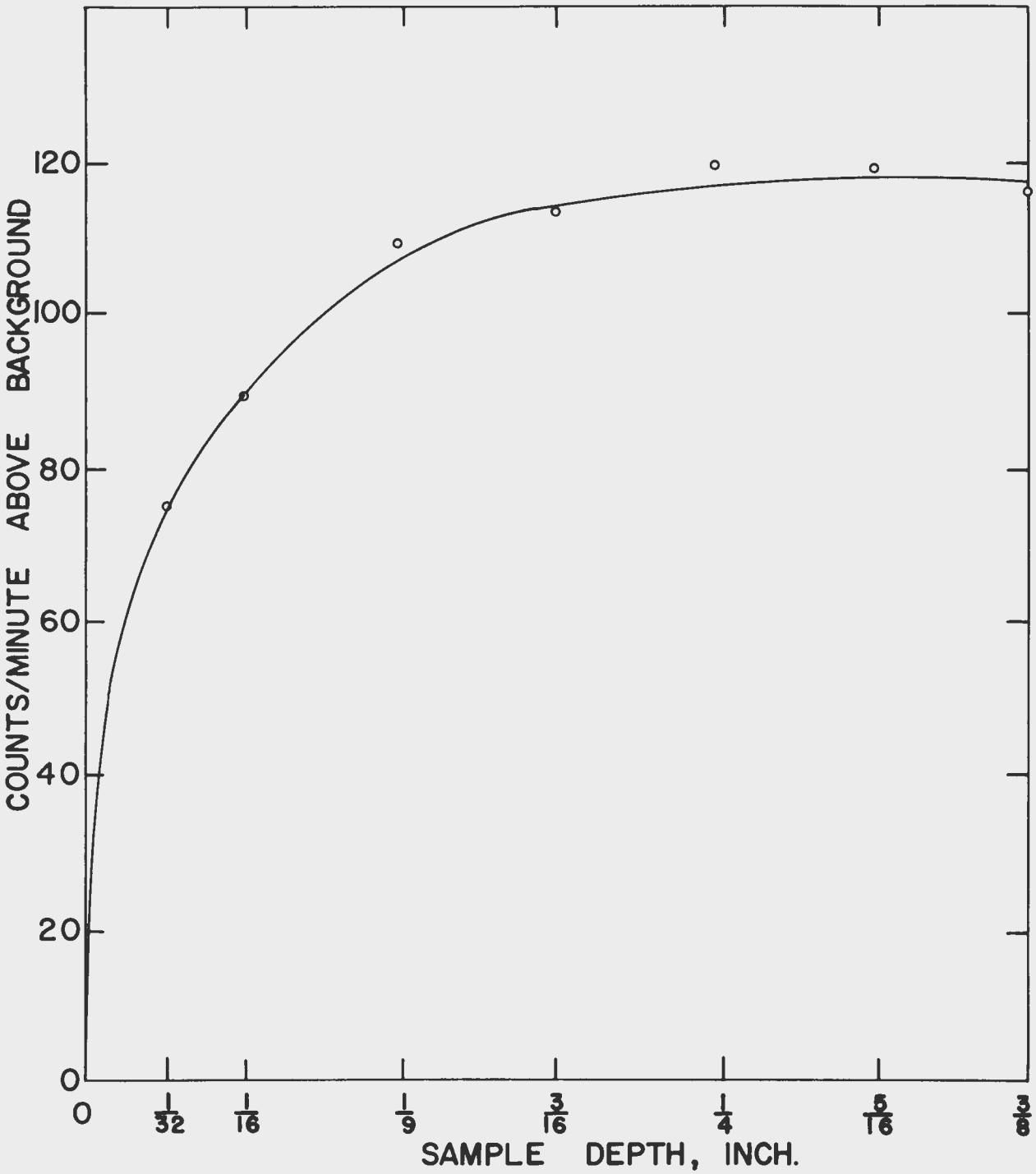

FIGURE 20. CORRELATION OF COUNTING RATE VS. SAMPLE DEPTH. REPRODUCED FROM DOIG. op. cit., PAGE 69.

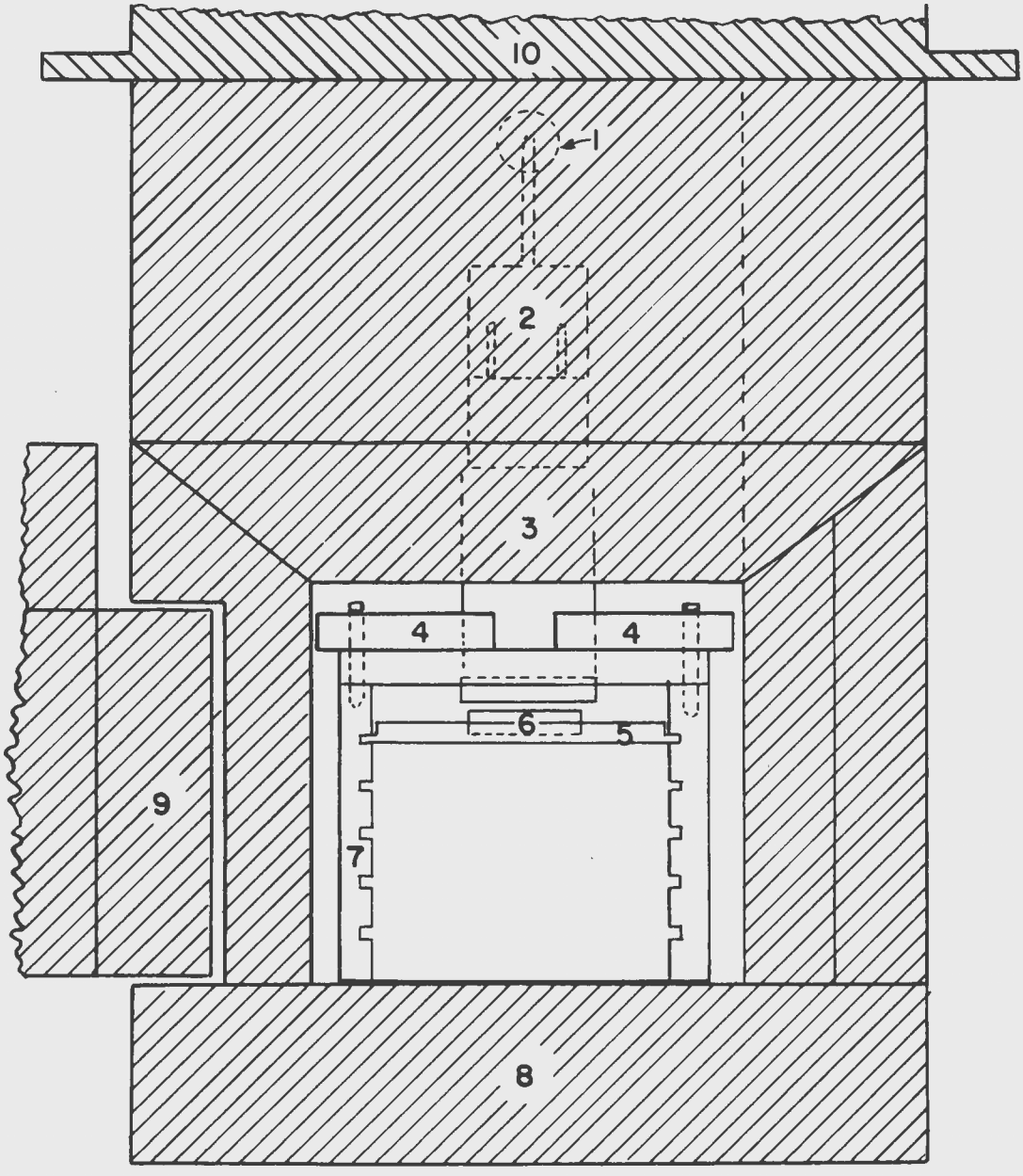

FIGURE 21. DETAILS OF RADIOASSAY SAMPLE HOUSING

1 CABLE OUTLET	6 SAMPLE PLANCHET
2 TUBE SOCKET	7 LUCITE SAMPLE HOLDER
3 G-M TUBE	8 CAST-IRON HOUSING
4 LUCITE TUBE CLAMP	9 HOUSING DOOR
5 SAMPLE HOLDING TRAY	10 HOUSING LID

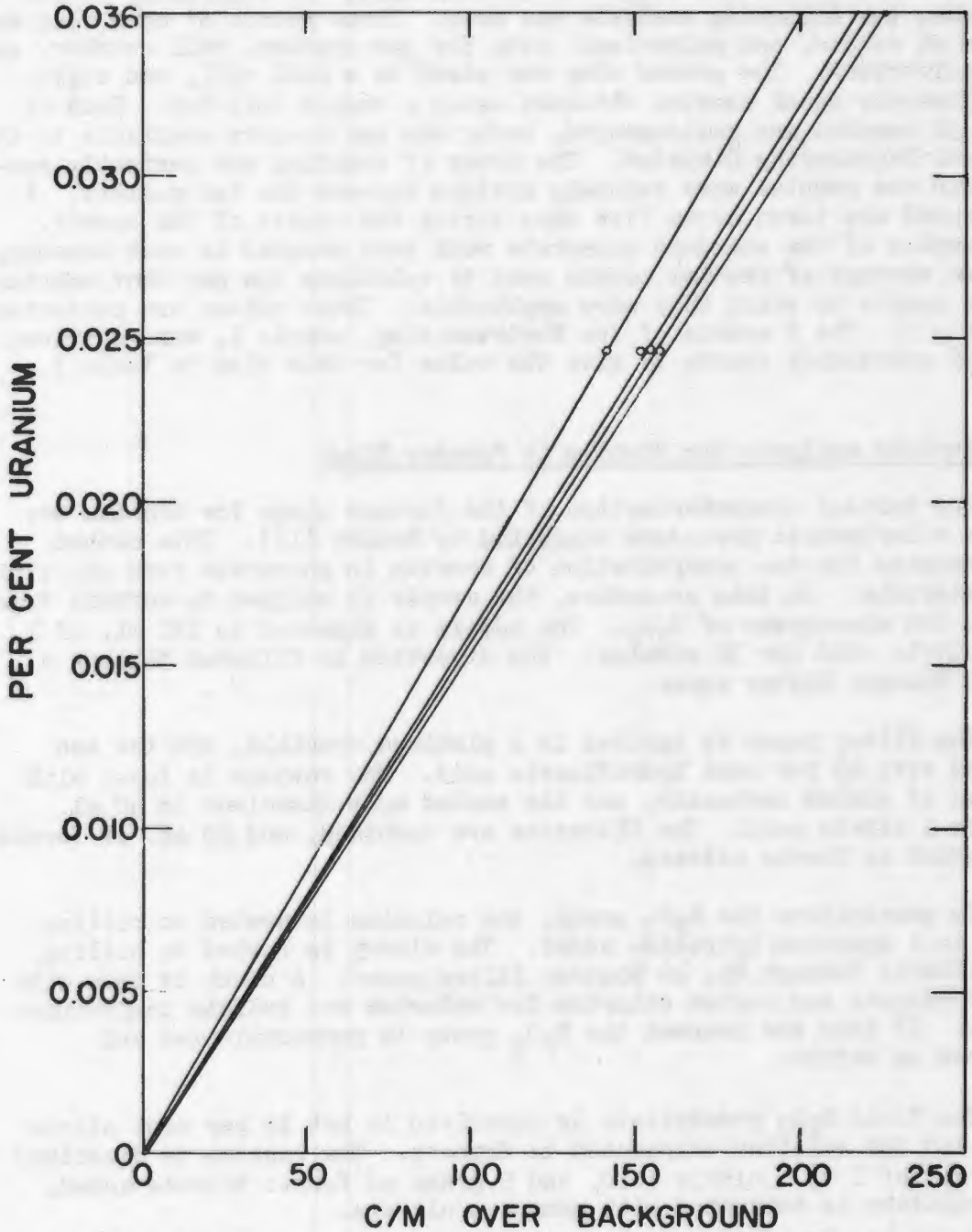

FIGURE 22. LINEAR CORRELATION BETWEEN PERCENT URANIUM AND COUNTING RATE OF STANDARD PHOSPHATE ROCK FOR SEVERAL REPLACEMENTS OF GEIGER–MUELLER TUBE

To characterize the slags for uranium using the radioassay method of analysis, the following analysis was made. Three pounds of each slag was chosen at random, and pulverized with the jaw crusher, roll crusher, and disc pulverizer. The ground slag was mixed in a ball mill, and eight approximately equal samples obtained using a sample splitter. Each of these 32 samples was radioassayed, using the two scalers available in the Chemical Engineering Division. The order of counting was perfectly random, and the samples were randomly divided between the two scalers. A background was taken every five days during the course of the counts. Two samples of the standard phosphate rock were counted in each housing, and the average of the two counts used to calculate the per cent uranium in the sample to which they were applicable. These values are presented in Table 7. The 8 counts of the Westvaco slag, sample 1, were combined with 45 additional counts to give the value for this slag in Table 7.

Colorimetric Analysis for Uranium in Furnace Slags

The initial characterization of the furnace slags for uranium was with a colorimetric procedure suggested by Rodden (17). This method was designed for the determination of uranium in phosphate rock and similar materials. In this procedure, the sample is weighed to contain from 100 to 600 micrograms of U_3O_8. The sample is digested in 150 ml. of 1 to 5 nitric acid for 30 minutes. The digestion is filtered through a No. 40 Whatman filter paper.

The filter paper is ignited in a platinum crucible, and the ash treated with 48 per cent hydrofluoric acid. The residue is fused with 3 grams of sodium carbonate, and the cooled melt dissolved in 40 ml. of 1 to 1 nitric acid. The filtrates are combined, and 20 mg. of ferric iron added as ferric nitrate.

To precipitate the R_2O_3 group, the solution is heated to boiling, and 1 to 1 ammonium hydroxide added. The slurry is heated to boiling, and filtered through No. 40 Whatman filter paper. A check is made with silver nitrate and barium chloride for chloride and sulfate ion, respectively. If they are present the R_2O_3 group is reprecipitated and filtered as before.

The final R_2O_3 precipitate is dissolved in hot 10 per cent nitric acid, and the solution evaporated to dryness. The residue is dissolved in 40 ml. of 1 to 4 nitric acid, and 5 grams of ferric nitrate added. This solution is saturated with ammonium nitrate.

This nitric acid solution is extracted with a continuous ether extractor for 135 minutes. The ether containing the uranium is evaporated to dryness, and the beaker washed down with 15 ml. of 1 to 1 nitric acid. One ml. of 70 per cent perchloric acid, 3 ml. of sulfuric

acid and glass beads are added, and the solution heated until white fumes are evolved.

The sides of the beaker are rinsed down with not more than 30 ml. of water, and the solution made slightly alkaline with 1 to 1 sodium hydroxide. One ml. of 10 per cent sodium peroxide is added, and 2.5 more ml. of 1 to 1 sodium hydroxide. The total volume of the solution is diluted to 50 ml. with water. The solution is filtered through No. 40 Whatman filter paper, and read in the Beckman model DU spectrophotometer at 390 millimicrons, using 10 centimeter cells and a slit width of 0.03 mm. The blank solution for transmittancy comparison is prepared with 30 ml. of water made slightly alkaline with 1 to 1 sodium hydroxide, 1.0 ml. of 10 per cent sodium peroxide, and 2.5 more ml. of 1 to 1 sodium hydroxide. The amount of U_3O_8 is determined from a transmittancy-concentration curve obtained by developing the color with known amounts of uranium present.

The standard curve developed for the procedure is shown in Figure 23. The data for all colorimetric standard curves in this investigation were treated using the method of least squares. As this system follows Beer's law, the regression analysis for a straight line applies. For the slope of the straight line

$$b = \Sigma(x \log y) - \frac{(\Sigma x)(\Sigma \log y)}{n} \Big/ \Sigma(x)^2 - (\Sigma x)^2/n$$

where: b is the slope of the straight line on semi-logarithmic coordinates,

x is the micrograms of uranium,

y is the per cent transmittancy,

n is the number of knowns used to establish the correlation,

The line established by least square treatment, solved explicitly for x, has the equation $x = \frac{\log a - \log y}{b}$

where: a is the y intercept of the straight line plot on semi-logarithmic coordinates,

log y is the logarithm of the per cent transmittancy reading,

x is the micrograms of uranium.

To obtain the micrograms of uranium, the per cent transmittancy is either referred to a plot of the line on semilogarithmic coordinates, or applied directly to the equation. The micrograms of uranium obtained is divided by the sample weight to obtain per cent uranium. The values shown in

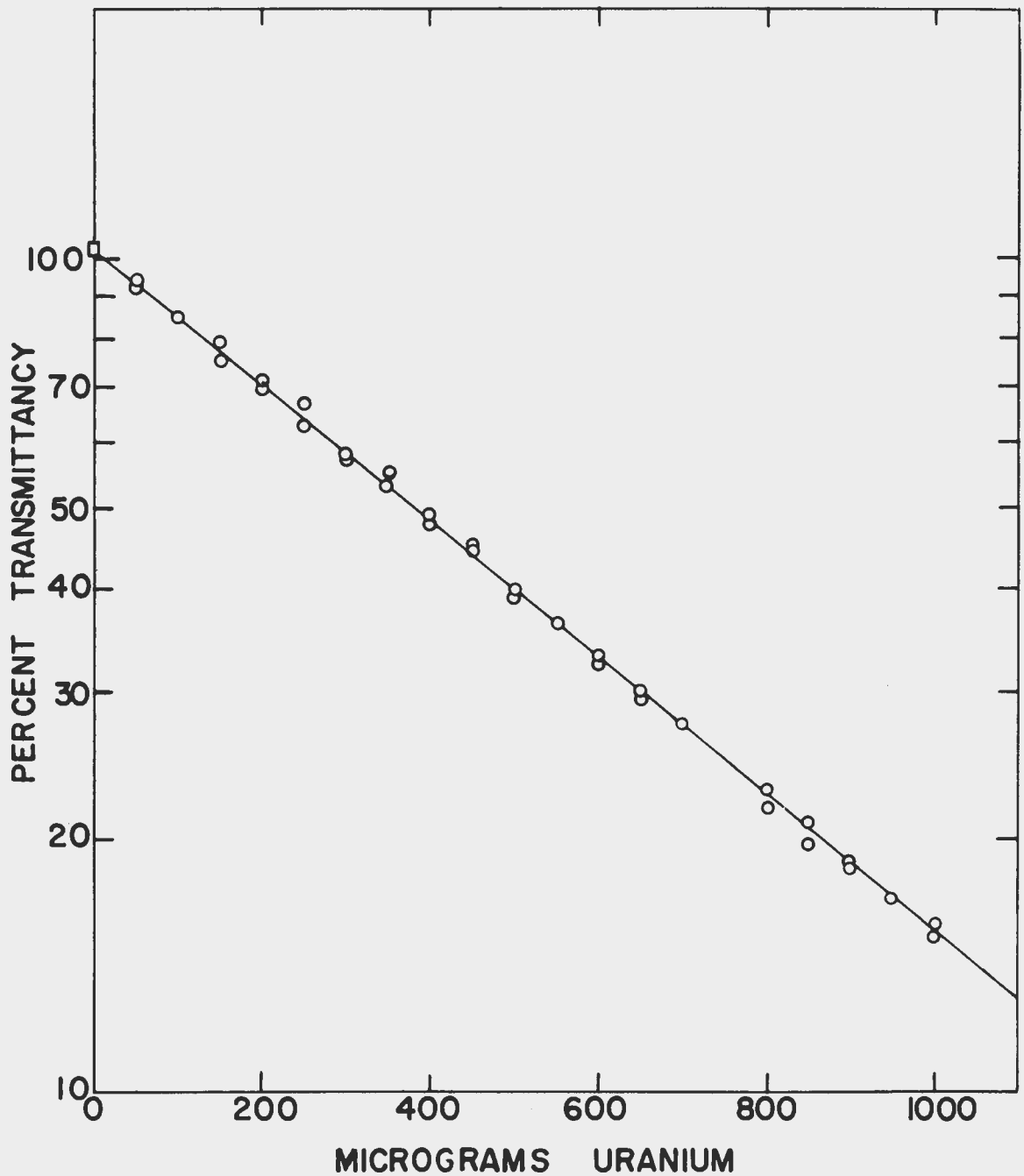

FIGURE 23. STANDARD CURVE FOR RODDEN NaOH—Na_2O_2 METHOD FOR ANALYSIS OF URANIUM IN PHOSPHATE ROCK

Table 7 for the Westvaco, sample 1, and Virginia-Carolina slags, using colorimetric method No. 1, were obtained using this procedure. The New Brunswick standard phosphate rock analyzed 0.026 per cent uranium by this method, based on three replicate analyses. Although the Rodden method seems to give high precision, and a highly sensitive standard curve, it is seen that the procedure is long, and not amenable to the rapid analysis of a large number of samples. An extensive study was made to make the procedure more rapid.

The procedure evolved was as follows:

1. A sample of material containing 100 to 600 micrograms of uranium was weighed out.

2. The material was digested on a hot plate in 50 ml. of 1 to 1 nitric acid and 25 ml. of 70 per cent perchloric acid for one hour.

3. 100 ml. of water was added and the solution warmed to take the metal salts into solution.

4. The silica residue was filtered off with No. 489 Blue Ribbon filter paper, and washed with 100 ml. of hot water.

5. The filtrate was transferred to a 600 ml. beaker, and 20 mg. of ferric iron added as ferric nitrate.

6. The solution was heated to boiling, and the R_2O_3 precipitated with 1 to 1 ammonium hydroxide.

7. The slurry was digested for ten minutes, and filtered through No. 589 White Ribbon filter paper.

8. The precipitate was washed with 100 ml. of cold water, and redissolved with 30 ml. of cold concentrated nitric acid.

9. The nitric acid solution was extracted for ten minutes with 30 ml. of 100 per cent tributyl phosphate.

10. The organic phase was stripped with two 15 ml. portions of 75 per cent saturated ammonium sulfate for five minutes each contact.

11. The strip solution was made slightly alkaline with 1 to 1 NaOH, and allowed to cool.

12. Two ml. of 10 per cent sodium peroxide and two more ml. of 1 to 1 NaOH was added.

13. The color solution was filtered through dry double No. 589 White Ribbon filter paper, and the total volume made up to 50 ml.

14. The per cent transmittancy was read in the Beckman spectrophotometer at 425 millimicrons, 0.03 mm. slit width, using a distilled water blank.

The standard curve using a distilled water blank at 425 millimicrons and 0.03 mm. slit width is presented in Figure 24. The conclusion is made that the method developed offered speed of analysis, but sacrificed sensitivity. The values shown in Table 7, for colorimetric method No. 2, as well as all analyses of experimental samples, were obtained using this method.

Colorimetric Analysis for Uranium in Alloys

Antimony-Uranium Alloys

Ten approximately 250 mg. samples of antimony metal were weighed. The metal was dissolved in 6 ml. of concentrated nitric acid and 25 ml. of concentrated hydrochloric acid. Uranium as uranyl nitrate was added according to the above schedule. The solutions were extracted for ten minutes with 30 ml. of tributyl phosphate. The organic phase was stripped with 75 per cent saturated ammonium sulfate for ten minutes. The strip solution was made basic with 1 to 1 sodium hydroxide. One ml. of 10 per cent sodium peroxide and 2 more ml. of 1 to 1 sodium hydroxide were added. The solutions were filtered through double No. 589 White Ribbon filter paper. The total volume was adjusted to 50 ml. with distilled water. The per cent transmittancy was read at 425 millimicrons, 0.03 mm. slit width, using the blue phototube, 1 cm. cells and a distilled water blank. The standard curve data are presented in Figure 25, with the best straight line established by the method of least squares.

To prepare the alloy for analysis, an approximately 0.25 gram sample of the sample was dissolved in 30 ml. of aqua regia. This solution was carried through the procedure described above.

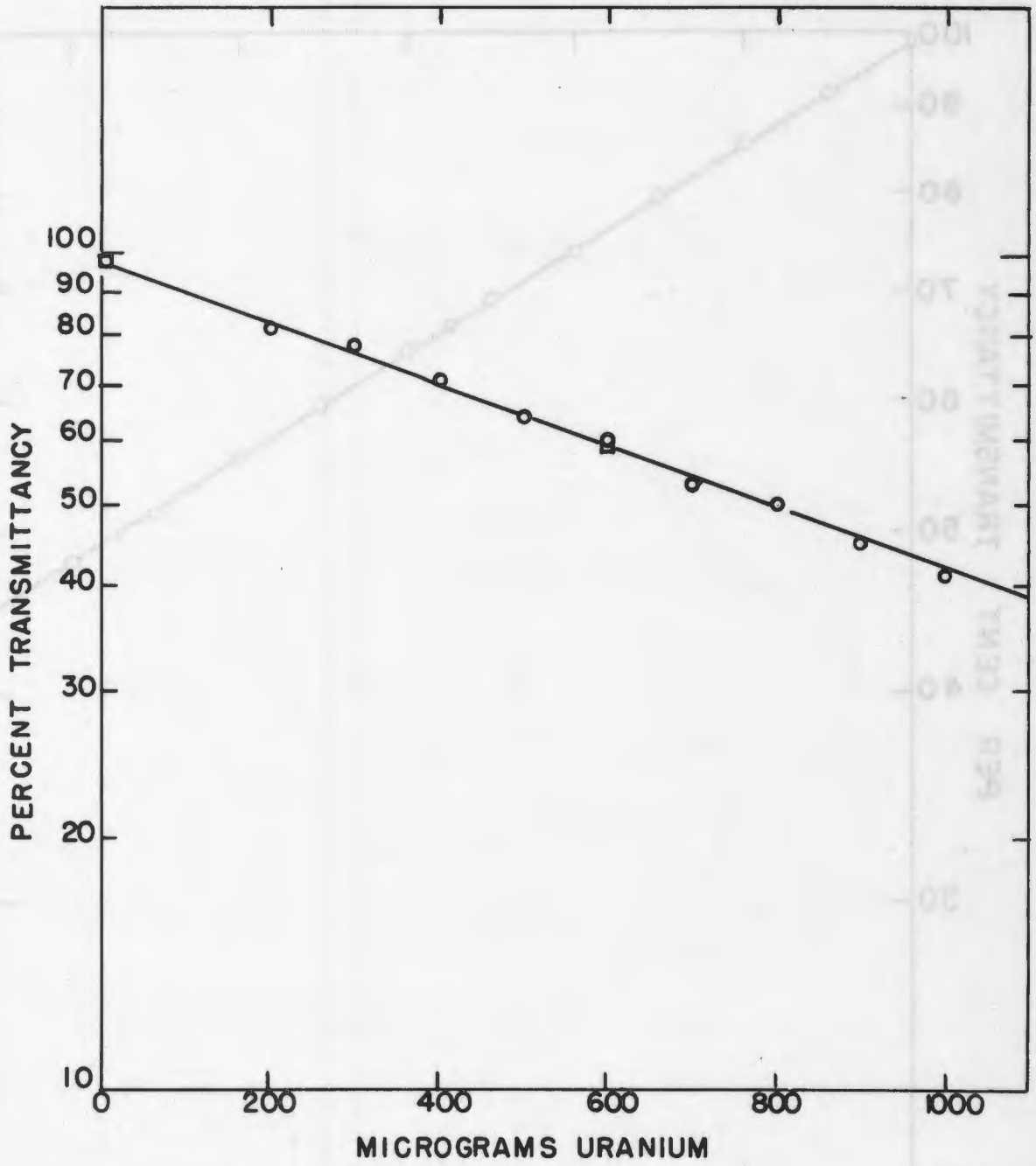

FIGURE 24. STANDARD CURVE FOR NaOH - Na_2O_2 METHOD FOR ANALYSIS OF URANIUM IN FURNACE SLAGS USING DISTILLED WATER BLANK.

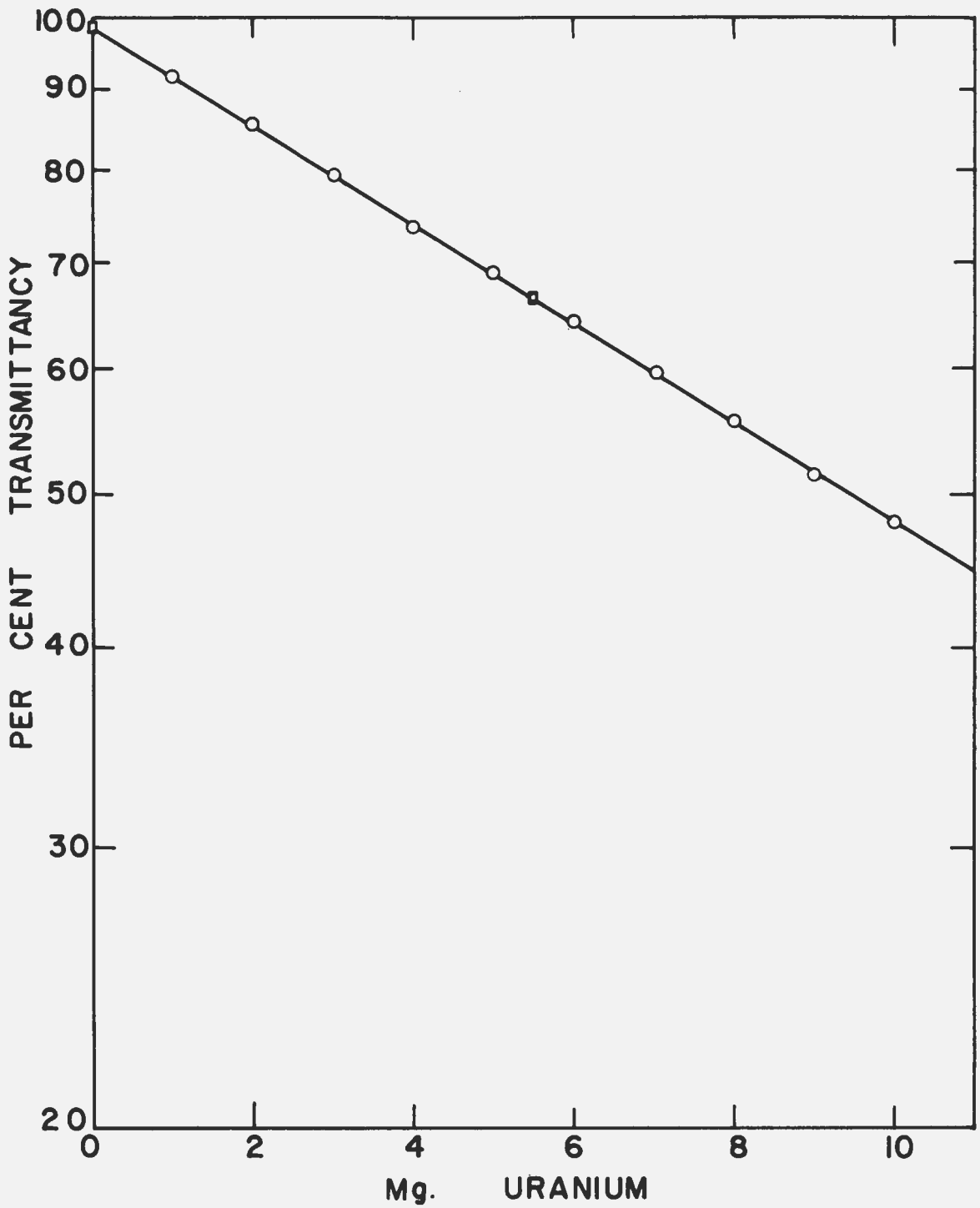

FIGURE 25. DATA AND REGRESSION LINE FOR ANTIMONY—URANIUM STANDARD CURVE

Bismuth-Uranium Alloys

Samples of bismuth metal were weighed approximately according to the following schedule:

No.	Mg. Bi	Mg. U	No.	Mg. Bi	Mg. U
1	240	10	6	190	60
2	230	20	7	180	70
3	220	30	8	170	80
4	210	40	9	160	90
5	200	50	10	150	100

The metal was dissolved in 5 ml. of concentrated nitric acid. Uranium was added as uranyl nitrate according to the above schedule. The total volume was adjusted to 20 ml. with distilled water, and the metals precipitated with ammonium hydroxide until the yellow color of U_3O_8 just appeared. Concentrated nitric acid was added to just redissolve the precipitated uranium, and 15 ml. of 10 per cent ammonium carbonate solution added. The slurry was filtered through double No. 589 White Ribbon filter paper, and the precipitate washed with 15 ml. of 10 per cent ammonium carbonate. One ml. of 30 per cent hydrogen peroxide was added, and the total volume adjusted to 100 ml. with distilled water. The per cent transmittancy was read at 425 millimicrons, 0.03 mm. slit width, using the blue phototube 1 cm. cells and a distilled water blank. The data for the standard curve are presented in Figure 26, with the best straight line established by the method of least squares.

To prepare the alloy for analysis, an approximately 0.25 gram sample of the alloy was dissolved in 5 ml. of concentrated nitric acid. The solution was carried through the procedure described above.

Lead-Uranium Alloys

Ten approximately 250 mg. samples of lead granules were weighed, and dissolved in 25 ml. of 1 to 1 nitric acid. Uranium was added as uranyl nitrate to give amounts of uranium from 1 to 10 mg. in the ten solutions. The solutions were extracted with 30 ml. of tributyl phosphate for ten minutes, and the organic phase stripped with 30 ml. of 75 per cent saturated ammonium sulfate for ten minutes. The strip solution was made basic with 1 to 1 sodium hydroxide, and 1 ml. of 10 per cent sodium peroxide added. Two more ml. of 1 to 1 sodium hydroxide was added, and the solution filtered through double No. 589 White Ribbon filter paper. The solution was adjusted to 50 ml. volume with distilled water, and the per cent transmittancy read at 425 millimicrons, 0.03 mm. slit width, using the blue phototube, 1 cm. cells and a distilled water blank. Figure 27 presents the standard curve data, with the best

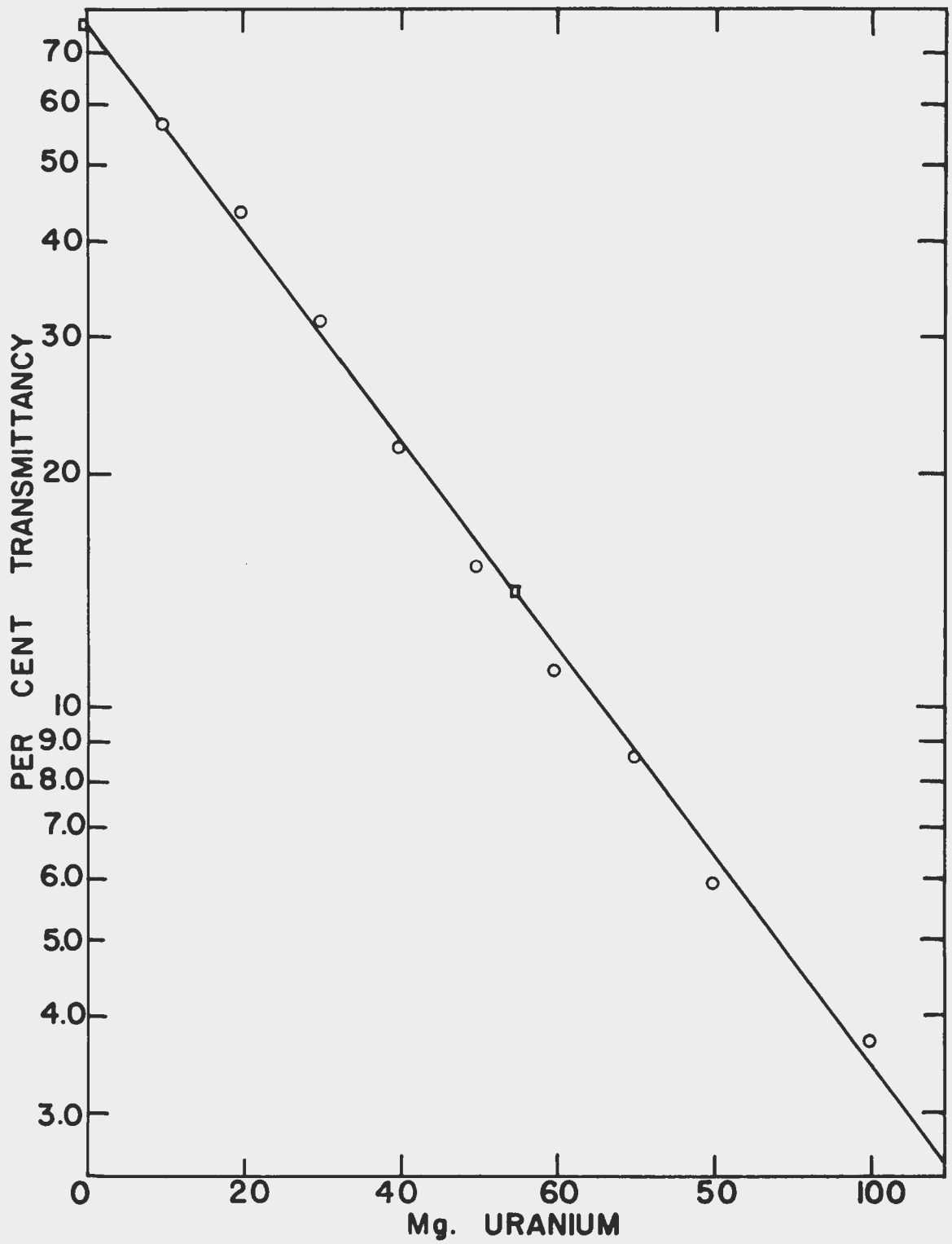

FIGURE 26. DATA AND REGRESSION LINE FOR BISMUTH—URANIUM STANDARD CURVE

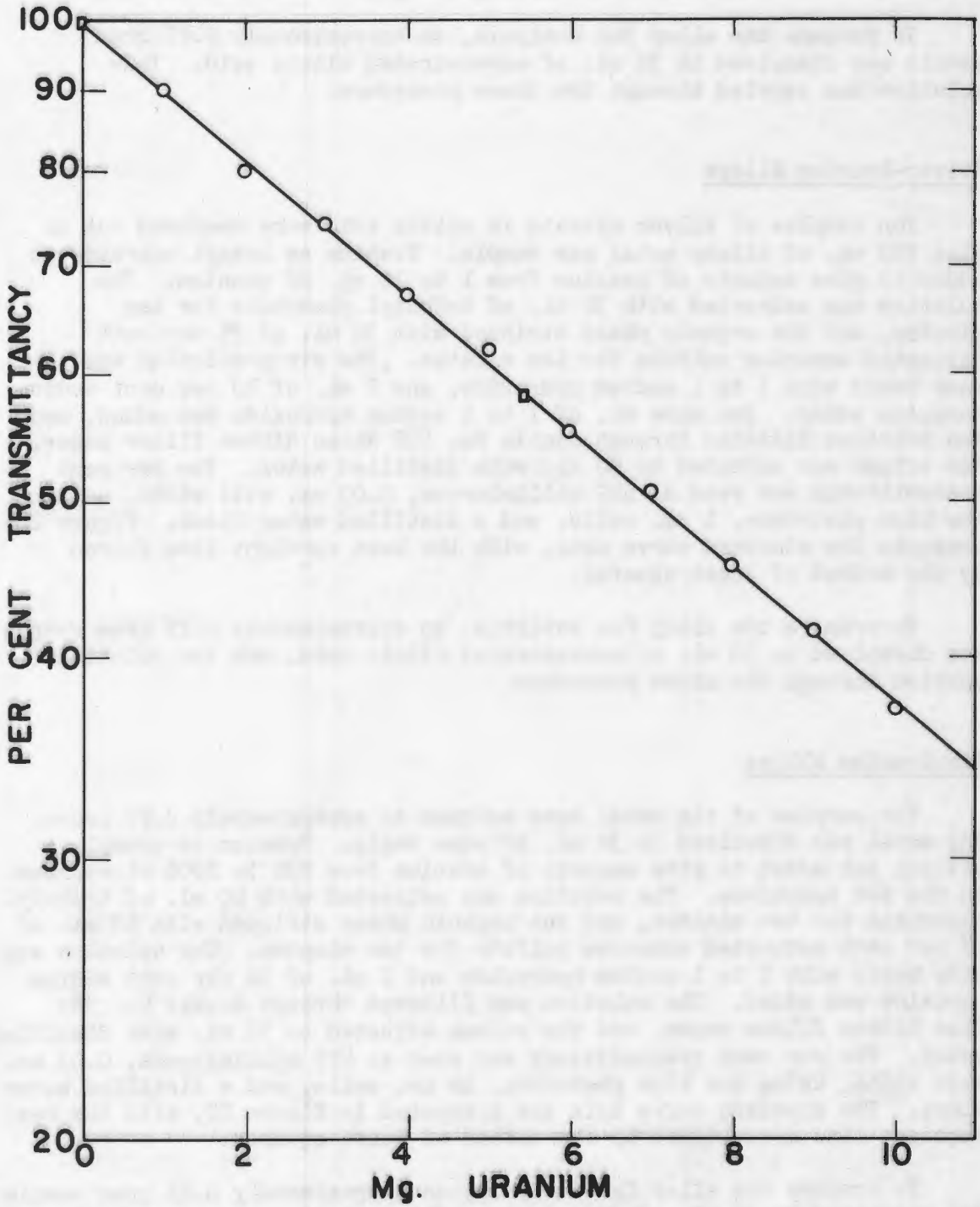

FIGURE 27. DATA AND REGRESSION LINE FOR LEAD — URANIUM STANDARD CURVE

straight line established using the method of least squares.

To prepare the alloy for analysis, an approximately 0.25 gram sample was dissolved in 30 ml. of concentrated nitric acid. This solution was carried through the above procedure.

Silver-Uranium Alloys

Ten samples of silver nitrate in nitric acid were measured out to give 250 mg. of silver metal per sample. Uranium as uranyl nitrate was added to give amounts of uranium from 1 to 10 mg. of uranium. The solution was extracted with 30 ml. of tributyl phosphate for ten minutes, and the organic phase stripped with 30 ml. of 75 per cent saturated ammonium sulfate for ten minutes. The strip solution was made basic with 1 to 1 sodium hydroxide, and 2 ml. of 10 per cent sodium peroxide added. Two more ml. of 1 to 1 sodium hydroxide was added, and the solution filtered through double No. 589 White Ribbon filter paper. The volume was adjusted to 50 ml. with distilled water. The per cent transmittancy was read at 425 millimicrons, 0.03 mm. slit width, using the blue phototube, 1 cm. cells, and a distilled water blank. Figure 28 presents the standard curve data, with the best straight line faired by the method of least squares.

To prepare the alloy for analysis, an approximately 0.25 gram sample was dissolved in 30 ml. of concentrated nitric acid, and the solution carried through the above procedure.

Tin-Uranium Alloys

Ten samples of tin metal were weighed to approximately 0.25 grams. The metal was dissolved in 30 ml. of aqua regia. Uranium as uranyl nitrate was added to give amounts of uranium from 200 to 2000 micrograms in the ten solutions. The solution was extracted with 40 ml. of tributyl phosphate for ten minutes, and the organic phase stripped with 40 ml. of 75 per cent saturated ammonium sulfate for ten minutes. The solution was made basic with 1 to 1 sodium hydroxide and 1 ml. of 10 per cent sodium peroxide was added. The solution was filtered through double No. 589 Blue Ribbon filter paper, and the volume adjusted to 50 ml. with distilled water. The per cent transmittancy was read at 425 millimicrons, 0.03 mm. slit width, using the blue phototube, 10 cm. cells, and a distilled water blank. The standard curve data are presented in Figure 29, with the best straight line established by the method of least squares.

To prepare the alloy for analysis, an approximately 0.25 gram sample was dissolved in 30 ml. of aqua regia. This solution was carried through the above procedure.

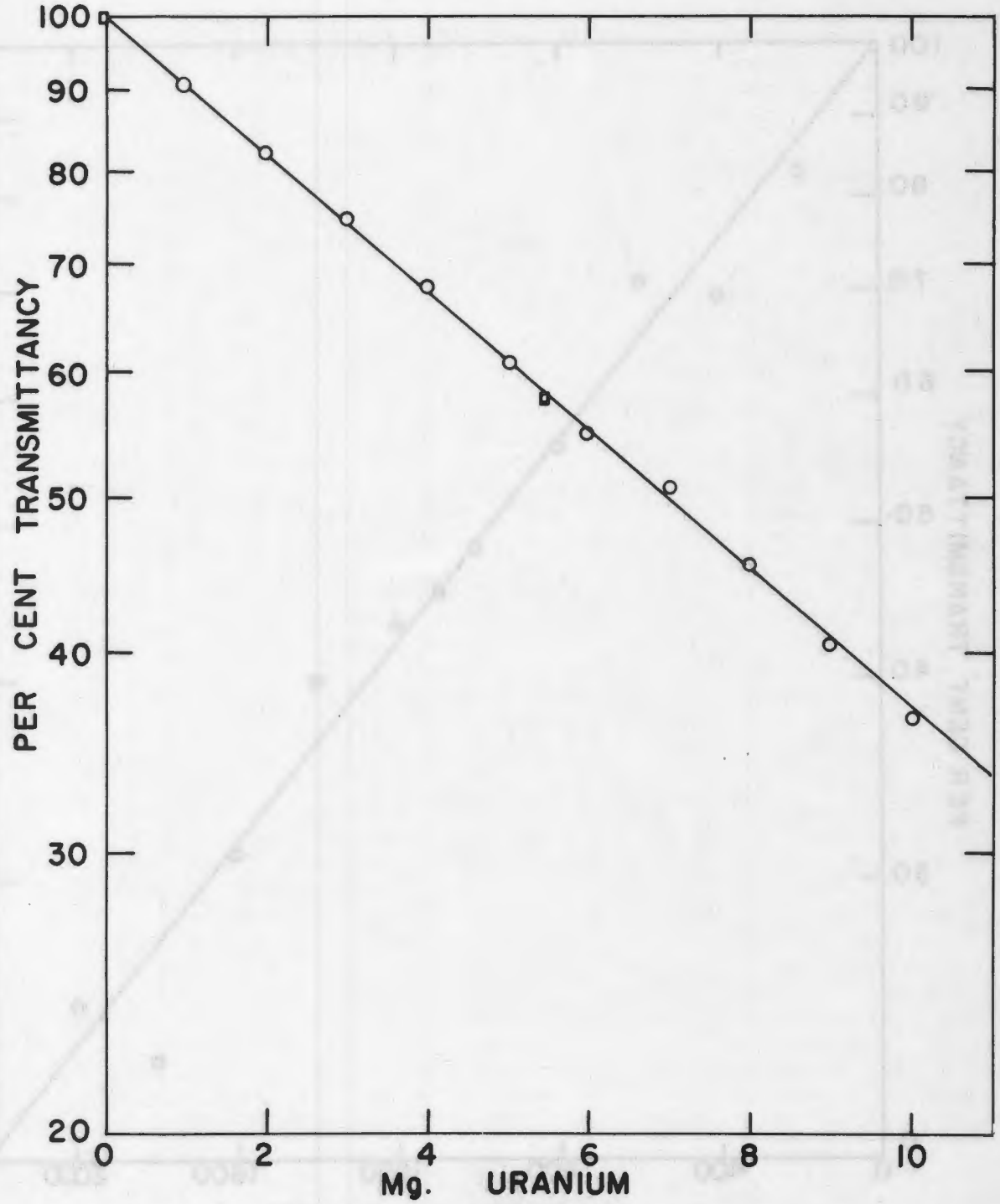

FIGURE 28. DATA AND REGRESSION LINE FOR SILVER—URANIUM STANDARD CURVE

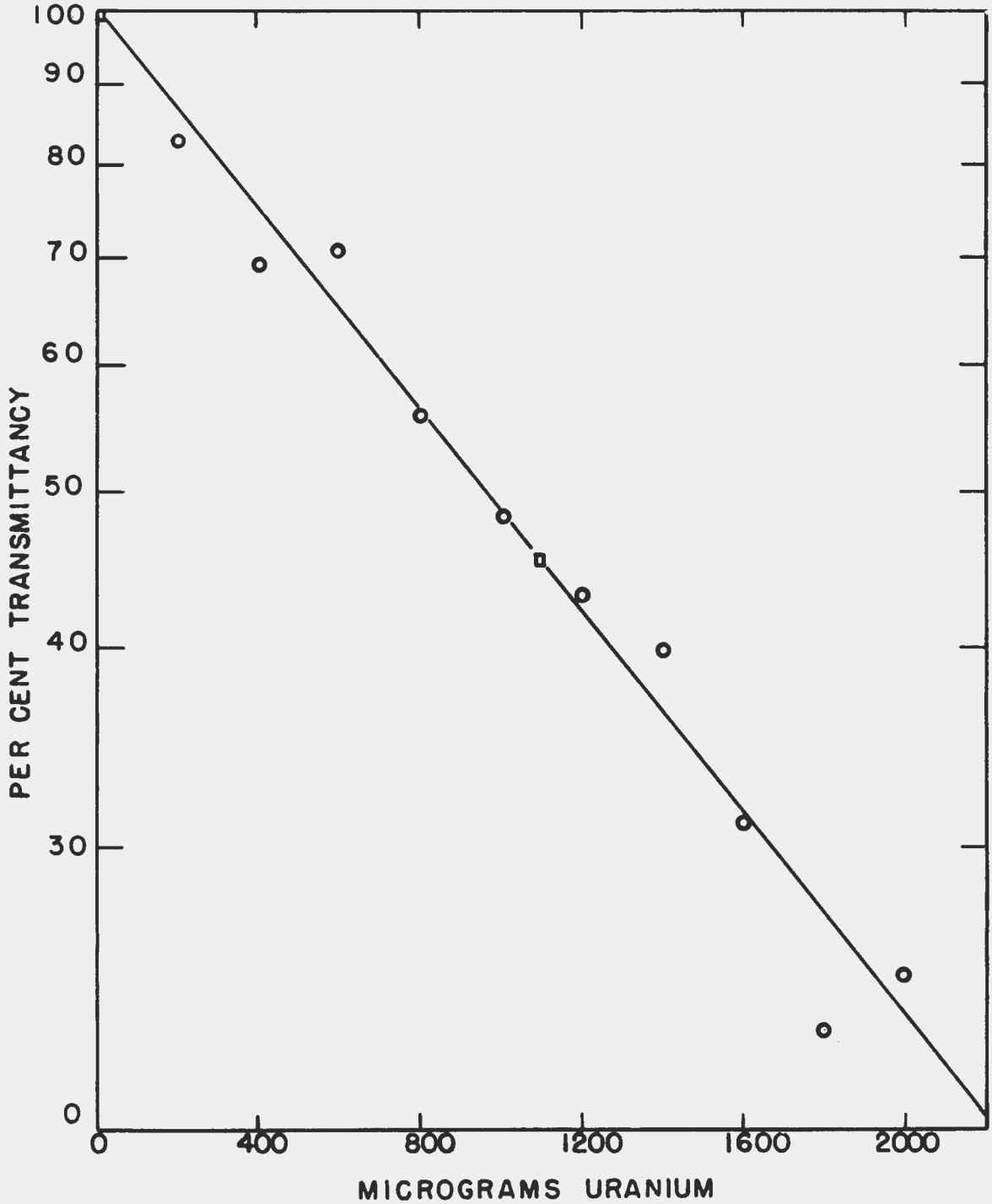

FIGURE 29. DATA AND REGRESSION LINE FOR TIN-URANIUM STANDARD CURVE.